BIOFUEL - PROCESS, NOVEL APPROACHES, FUTURE PERSPECTIVES

Abstract

An increasing population leads to an escalated usage of vehicles, which in turn fosters a situation to utilize these conventional fuels (namely petrol, diesel, and natural gas) at a high rate. This leads to the diminution of natural resources, in addition to the statement, an enhanced level of greenhouse gases in the atmosphere yielding Global Warming. To alleviate these consequences. There is a need for the production of some other non-conventional resources as a backup or any other alternative fuel. Here comes the role of Biofuel as an alternative fuel. These biofuels are sorted out into different groups based on their sources. This field of biotechnology has numerous scopes in the forthcoming years. It had crossed the paths of its development that is near to a century. This chapter discloses in detail the biofuels, sources, and case studies in the production of biofuels or explains the recent approaches such as optimizing the production, utilizing novel substrates, and modifications made in the bioreactor design for the improvements in the yield. This chapter also includes novel catalysts used for the production process and also comprises techniques for the extraction of biofuels from a reaction mixture short. The measuring parameters to evaluate the performance of biofuels in engines and the considerations to be checked are described. The applications of Nanoparticles and their effects in improving the efficiency of biofuel production were explained in this chapter.

Keywords: Biofuels, Nanoparticles,

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I. INTRODUCTION

All over the world, different countries organize conferences and summits to outsource the proposals for the production of these categories of non-conventional fuels that are sourced from various biomass sources or any other biological substances. Countries such as North America, Europe, and Southeast-Asian countries are working on the large-scale manufacturing of these biofuels from life sources. As reported in the survey by the year 2022, the top ten countries that steer them to indulge in biofuel production frequently are known to be the USA, India, China, Brazil, Malaysia, Italy, the UK, Indonesia, Iran, and Australia. The race still goes on in the increased production of biofuel in all parts of the world. Then there is a widespread technology that leads to the use of distinct varieties of biomass samples in different parts of the world by the application of diverse cum novel methodologies. In addition to that, the samples that are used for the production of these fuels by the implication of samples that are from wastes or the by-products of agricultural products.

Biofuel is a tangible option for the choice of eradicating the utilization of fossil fuels and has helped us to overthrow the extent of the fossil fuels-based society. Biofuel is the prevailing solution for decarbonizing the global environment and in the decrement of temperature around the globe by 2°C, as a consequence of the reduction in the amount of greenhouse gases to the level of ~43%. The study of R. Zah *et al*, 2009, (3) concluded the ways to ameliorate biofuel sustainability. The scientists have developed an evaluation of the biofuels and their environmental aftermaths and also disclosed the ideas for biofuel standardization and contrivances for certifications. The studies included in this special issue illustrate that the expansion of biofuel production is intricately associated with the global trading prospects of biofuels. The impacts are multifaceted and heavily influenced by policy measures. Consequently, assessing the comprehensive global effects of trading biofuels on the environment and the global economy remains challenging. However, some of the collective findings from the study were some of the interpretations can be taken up to mitigate negative impacts and harness the potential use of these biofuels in forthcoming years.

1. Policy steps are made to play a pivotal role in driving biofuel production and utilization. However, the outcomes of these policies vary significantly based on the market circumstances prevailing globally and the interactions with the other doctrines.

2. Biofuel production was closely intertwined with the market for food and feed commodities. The above interrelation arises from competition for agricultural land, primarily for reasons beyond feedstock. To ensure sustainability, future biofuel production should minimize competition for land and then it relies more on residual materials.

3. Small-scale projects are developed for the production of bioenergy and generally offer benefits for both the environment and as well as to society with very minimal levels of risk. Conversely, projects that tend to carry greater economic risks, and their social benefits might be less positive.

4. Efforts are being made to develop globally recognized, transparent, and easily implementable certification schemes. These schemes are essential prerequisites for the widespread adoption of sustainable biofuels on a global scale.

II. BIOFUEL- GLOBAL MARKET

Post COVID-19 Pandemic and the Ukraine- Russia War, in the year 2022, biofuel production faced a crisis of downfall in the supply levels of 1st generation feedstock supply, as Russia plays a crucial role in the supply of 1st generation feedstocks such as sunflower oil, wheat and maize and also the fertilizers for the agro market development. This developed the circumstances to reach out for the different novel feedstocks such as bio-based wastes, algal biomass, and food wastes, genetic engineering in feedstock improvements and resulted in the processing cum production of 2nd Generation Biofuels. Later, 3rd and new-generation biofuels are manufactured to meet the needs of the fuel necessities around the globe. This choice of feedstocks has contributed to the reduction of carbon emissions, greenhouse gas emissions, and Global temperature, and has inculcated a culture of utilizing agro and food wastes, valorization of resultants of certain biologically processed by-products from the industries globally. (4) Figure 1 depicts the diagram representation of the Global Biofuel market.

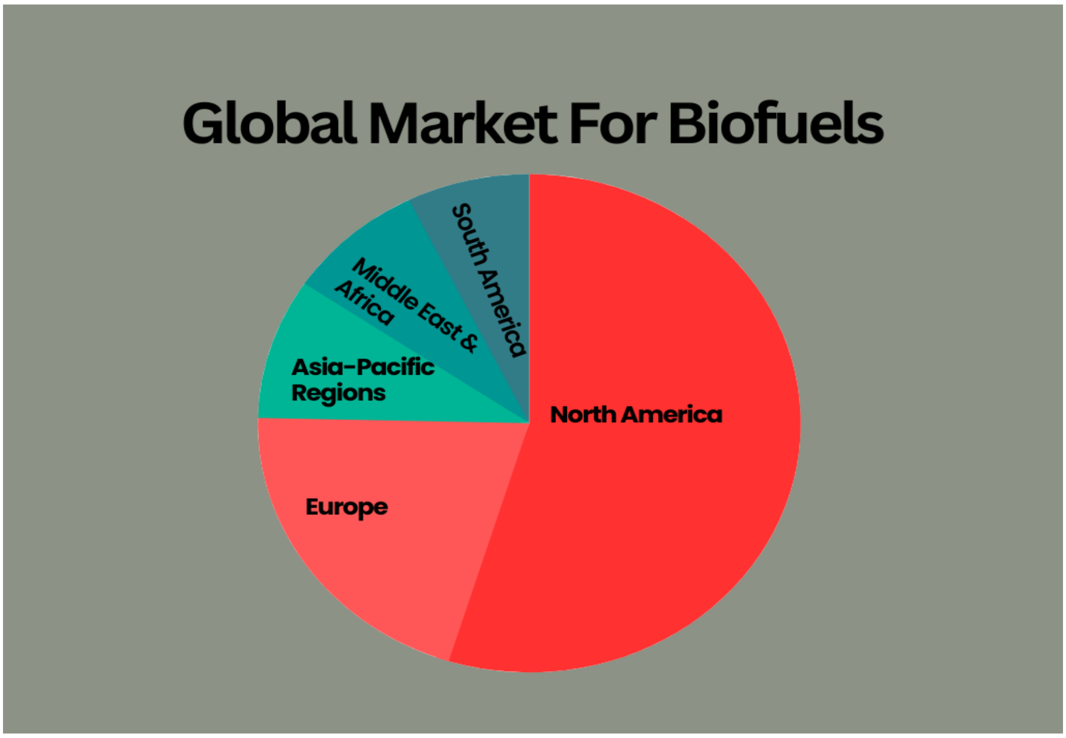

Figure 1: Pie Diagram Representation for Global Biofuel Market

III. SOURCES OF BIOFUELS

Primarily, biofuels are produced from biomass sources or by-products of various plant sources that were the residues of agricultural activities. The sources are forest residues (such as firewood, and wooden chips) and farm residues (such as leaves, grasses, and weeds). These are classified as primary sources for the production of biofuels. Certain food crops are being implemented for biofuel production. The starch present in the sugarcane stems and beets, for the oils present in the seeds of sunflower, rapeseed, and soybeans is being fermented for bio-alcohol and bioethanol manufacturing. The crops chosen are to be plenteous in sugars, starch, and oils. Then plant sources such as silver grass

(*Miscanthussinensis*), Nettlespurges (*Jatropha curcas*), Elephant grass, switchgrass, and Cassava (*Manihotesculenta*), which are applied for the production of bioethanol by the novel sources of the starch, oils, and sugars using the conventional technologies. In addition to the above lines, sources that possess lignocellulose yield the syndiesel. These substrates are processed along with the microbes to yield the biofuels. The biofuels are even produced from the algal species such as microalgae and seaweeds.

Based on the types of substrates used for biofuel production, the sources are sorted under two titles namely Primary and secondary biofuel sources. In addition, the secondary class of substrates is then categorized into discrete three classes namely, first, second, and third classes for representing these substrates. Correspondingly, the biofuel products from these sources or substrates can termed as first, second, and third biofuel generations as well. Now new generation classifications of biofuels are produced by utilizing plastic wastes. Research is in still progress to generate biofuels onan industrial scale at very high volumes (2).

IV. BIOFUELS- CLASSIFICATION

The categorization of biofuels is done based onthe types of sources used for the production of these fuels (22). The chart (Fig 2) represented below throws an idea to classify the biofuels, namely,

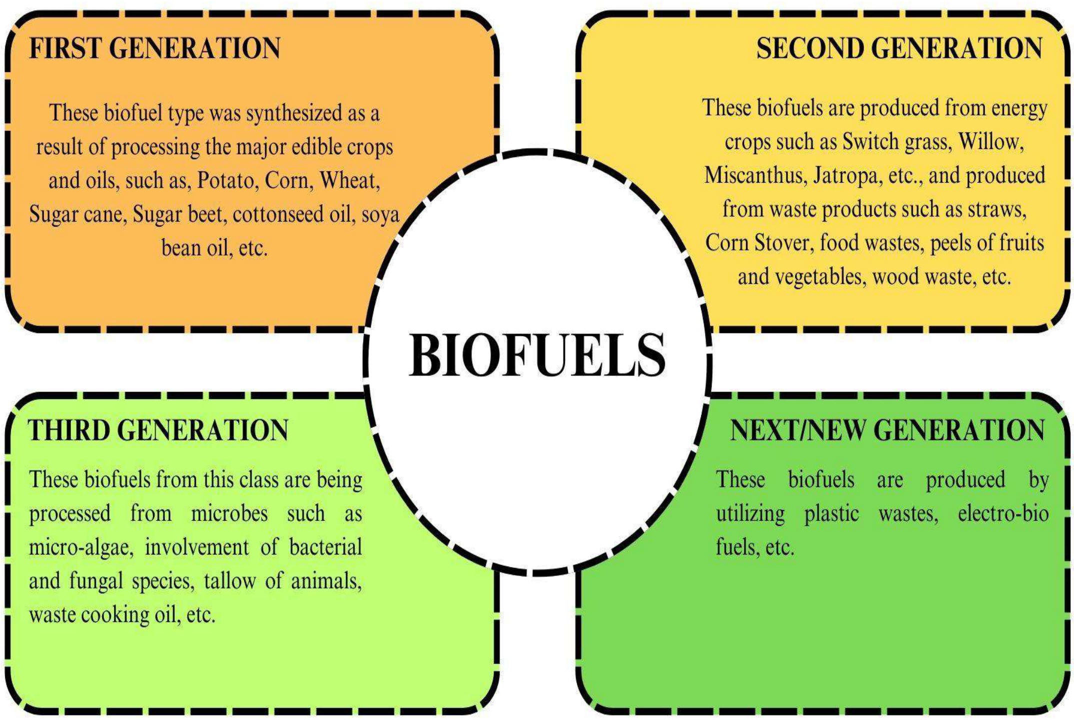

Figure 2: Classification of biofuels

Biofuel-Classification

First Generation Biofuels: These biofuels are produced from major edible crops and oils such as Potato, Corn, Wheat, Sugar cane, Sugar beet, cottonseed oil, soya bean oil, etc.	Second Generation Biofuels: These biofuels are produced from energy crops such as Switchgrass, Willow, *Miscanthus*, *Jatropa*, etc., and produced from waste products such as straws, Corn Stover, food wastes, peels of fruits and vegetables, wood waste, etc.
Third Generation Biofuels These biofuels are derived from microbes such as micro-algae, involvement of bacterial and fungal species, tallow of animals, waste cooking oil, etc.	Next/New Generation Biofuels: These biofuels are produced by utilizing plastic wastes, electro-bio fuels, etc.

V. PROCESS STEPS INVOLVED IN BIOFUEL PRODUCTION: A FLOW REPRESENTATION

The biofuel production process involves the pre-treatment or processing of feedstocks in the preliminary stages for the retrieval of oil from the biomass fed to the reactor system. Then the involvement of process parameters such as methanol, catalysts, and reaction conditions favor the reactions involved in the conversion of biomass to oil and then proceed with further processing steps undertaken for the production of desired biofuels. For that, initially, the biomass is treated by undergoing processes such as thermo-chemical processes and biochemical conversions (Fig 3).

The thermos-chemical process includes methods such as pyrolysis, gasification, and liquefaction, and the bio-chemical conversion takes place by the application of methods such as anaerobic digestion and fermentation. Pyrolysis is an anaerobic process that in the breakdown of long fatty acid chains by the application of heat at very high-temperature scales. Pyrolysis can be classified under different types of pyrolysis processes based on the rate of the reaction for production, such as fast and slow methods of the pyrolysis operation. Here, pyrolysis in slow mode (i.e., Slow Pyrolysis) is termed as Carbonization. This pyrolysis process is widely applied in the production of biofuels.

Gasification is the process involved in the incorporation of biomass to result in energy-rich gaseous products or fuels. Liquefaction is involved in the conversion of provided biomass into liquid hydrocarbons of high stability under low temperatures and high pressures.

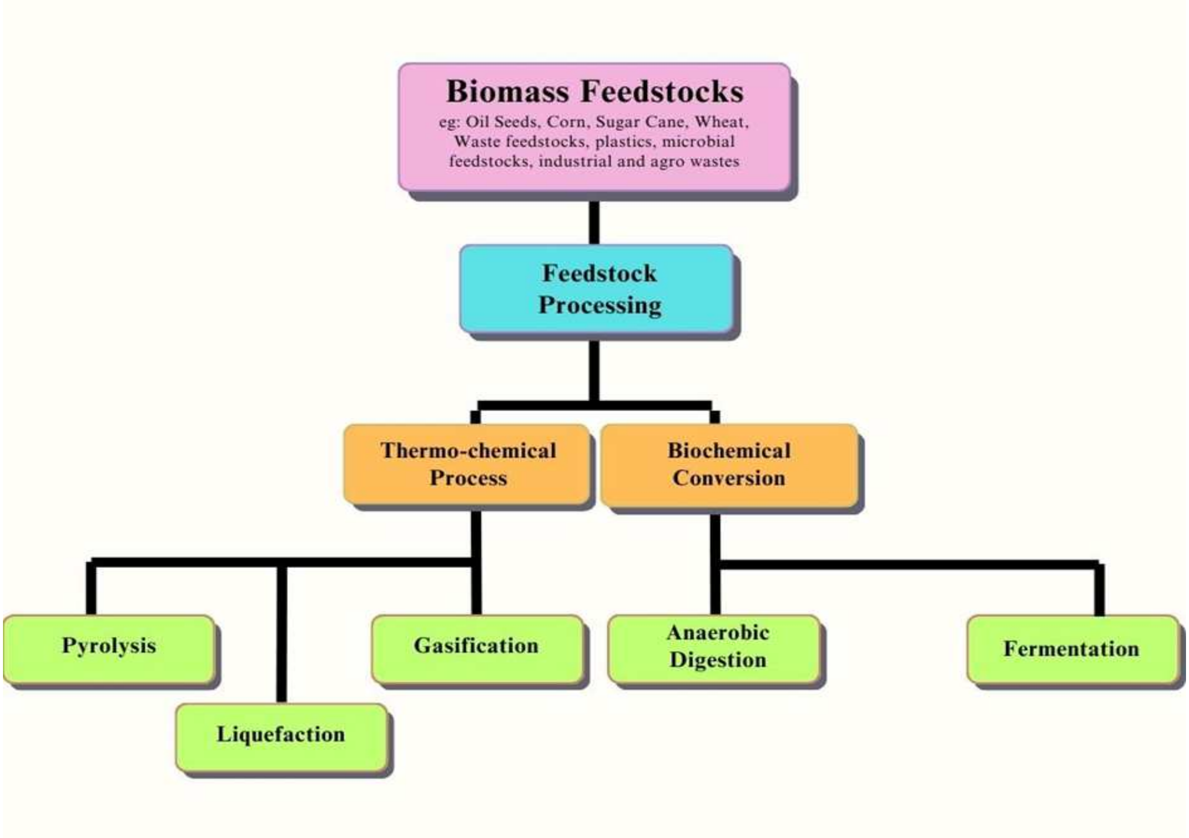

Figure 3: Methods applied for Biomass Processing

VI. CASE STUDIES: NOVEL APPROACHES IN BIOFUEL

1. Novel Bioreactor System in Biofuel Production:

- **Biofuel Produced from Bionic Flow-induced Peristaltic Reactor:** Wang et al (2022) performed a novel study in improvising the production yield of the biofuel produced by constructing an efficient novel structured reactor named bionic flow-induced peristaltic reactor was constructed and readily applied. It seemed to be a tubular reactor type. In this study, the group worked on the production of biofuel from soybean oil was used as a chief substrate.The reactor showed a result of high-efficiency mixing, a higher rate of conversion of the substrates (soybean oil) into biofuel, and excellent mass and heat transfer attributes. This system functions based on the virtue of interactions between the walls of the fluid and the internal fluid flowing through the tube. These interactions tend to enhance the agitation of the fluid at a higher rate. The functioning of this system enhanced the properties of the heat and mass transfer are concluded by this investigation. The realistic conditions of the peristalsis motion inside this novel reaction system were first designed and analyzed under the method of dynamic simulation by the mathematical and physical model. Later the reactor was built experimentally and noted.

- **Materials Involved:** The prime source of the biochemical reaction that needs to be converted is Soybean Oil, which was first procured from the Meryer Chemical Technology Company situated in Shanghai, China. Soybean oil possesses a composition of various fatty acids which include Palmitic, Oleic, Linolenic, and Stearic. In addition to the soybean oil, the materials included in the composition of the feedstock, that get involved in the reaction are Methanol, Sodium Hydroxide, Ethyl acetate, and Hydrochloric acid. In this study, the chemicals used for the reaction are of analytical grade.

- **Simulation Methodology:** In this novel reactor, the fluid flow through the pipe causes the wall deformation of the tube. Correspondingly, as a result, the tube exerts pressure on the fluid affecting the flow patterns of the fluid, this causes the mixing of the substrates. Thus, it is involved in the significant improvements in the performance of the mixing. Furthermore, clarification of the intermixing of the fluids inside the reactor and the reactor wall deformation is calculated by the Three-dimensional modules of the Simulation process for the reactor was carried out by the system software named ANSYS Platform. Here the simulation of the Solid domain was carried out by the Mechanical and the fluid domain simulation was carried out by the Fluent and then the System Coupling Module worked on the fluid-solid data exchange. Earlier, the parameters such as the diameter of the outlet and the inlet of the elastic tube of the peristaltic reactor were 10 and 4 mm respectively. An interface system, the System Coupling Module works by the methodology of the Separate Solution Method, helped to calculate the domains of fluid and solid discretely at disparate time intervals. The results are converged for the final output.

- **Cultivating Biofuels through Dividing Wall Column (DWC) Technology:** Distillation has played a prime role, from the beginning of biofuel production, in the extraction of biofuel from the processed feedstock. It was furtherance in the production process that promoted favorable conditions to use the biofuel yield. This dividing wall system can be applied industrially, which had manifested for its large-scale or industrial-scale production. This technology was employed for multi-component separations and various distillation types which comprise techniques such as azeotropic distillation, reactive distillation, and extractive distillations by constructing the DWC in terms of Simple DWC, DWC utilized for the reactive mode of distillation (R-DWC), DWC combined with azeotropic distillation process(A-DWC), DWC with Extraction distillation experimentation (E-DWC) respectively. These columns are exploited to work for the tasks for the processes including the synthesis of FAME which can be abbreviated as Fatty Acid Methyl Esters and then for the production of the DME which stands for the compound Dimethyl Ether using the R (Reactive)-DWC system and had involved in the efficient recovery of methanol and glycerol, a consolidated approach of DME purification with the simultaneous recovery of methanol and CO2, during the production of biodiesel and bioethanol.

- **Reactor- Experimental Setup and Working:**

- **Peristaltic Reactor: Construction& Working:** The reactor system was equipped with 3-6 identical segments of peristaltic tubes of similar dimensions. These tubes are soft, flexible made of materials such as rubber which has an easy deforming tendency and is capable of creating the phenomenon of peristalsis. Every peristaltic segment of the reaction system possesses an elastic peristaltic tube, a fixed rigid tube, and a holding stand with a clamp and these components of the reactor are enveloped inside a firm outer casing. The whole peristaltic reaction system is of the length 60cm and the individual peristaltic tube is 6cm in length. Then the thickness of the wall of the soft tube is 0.5mm. This reaction system consists of a storage tank for the feedstock, a central controlling system, a peristaltic pump, and a pressure regulator unit. Using the peristaltic pump, the feedstock containing soybean oil was pumped into the reaction system (a reactor) from the feed tank with the help of the pulsating pressure created by the pump. This made the sections of the peristaltic pump expand and contract in a periodical way enabling the substrate mixing at a higher rate. The system for temperature control comprises a thin heating element in the structure of a film and a temperature control unit, which checks out and regulates the temperature favorable for the reaction inside the reactor, which can help to attain a high rate of conversion. The pressure-controlling or regulating device that was placed at the outlet was involved in bringing the peristaltic amplitude to a desired size and also assisted the variation of the peristaltic period by the adjustment of the pulsating pressure cycle.

- **Experimental Procedure:** In this experiment, the biofuel produced was biodiesel in a Batch mode of operation, which was performed in a 200ml capacity glass-made conical flask reactor that was fastened to an air-bath or shaker bath system. An incubator is equipped with a rigid tube reactor and a bionic peristaltic reaction system. For comparison, the rigid tube reactor possessed a cumulative length of 60cm. Within this peristaltic reactor, the conversion of biomass into biodiesel takes place. This reactor was built to examine the reaction efficiency and the effect of peristalsis in the production of in conclusion, this novel reactor showed a high rate of conversion.

- **Dividing Wall Column:** Working The DWC unit was fed with the feedstock, into the pre-fractionator, and the side stream was retrieved from the other side of the column. The collected side stream was comprised of mid-boiling constituents, the lightest constituent from the feed gets vaporized and eliminated through the top and the heavy constituents get down to the bottom of the column favoring the separation. The DWC system showed a high range of purity of the fuels extracted in the same unit and resulted in a minimal temperature difference between two walls, it provides a clear view of the accomplishable implementation with a minimal heat transfer and an insignificant effect on the performance of the column. This experimentation elaborates on the role of this DWC in the industrial production of biofuel. This novel construct is capable of decreasing the capital invested and minimizing the energy requirements up to 17%. By performing methanol and glycerol recovery in the same reaction unit, 27% of the energy was conserved. R-DWC setup had inflated the levels in the synthesis of FAME, which in turn reduces the steps in the process flow and manifested a rigorous reduction in the energy usage for each unit operation performed, also the DME synthesis by R-DWC resulted in the reduction of 60% energy consumed and also the costs for operation. Distillation (azeotropic or extractive) along with DWC made the pre-concentration and dehydration of Bioethanol in a single step.

Table 1: **Physical Parameters and Considerations for the Reactor System**

Parameters Of the Reactor	Unit	Rigid Reactor	Peristaltic Reactor
Thickness of the reactor or tube wall	mm	0.5	0.5
Diameter- Outlet	mm	9	9
Diameter- Inlet	mm	4	4
Fluid Temperature- Cold fluid	K	273	273
Fluid Temperature- Hot fluid	K	353	353
The material used for the Wall	-	Stainless Steel	Rubber
Viscosity of the Fluid (Feedstock)	m.Pa.s	1 to 400	1 to 400
Poisson's Ratio	-	-	0.47
Young's Modulus	Pa	-	3 x 10^6

A different study utilized a newly designed bioreactor for the production of biodiesel. This bioreactor consisted of two distinct components: a pre-treatment reactor, similar in design to a stirred tank reactor, and a continuous operation packed bed reaction system. To facilitate the conversion of biodiesel, an immobilized form of a lipase enzyme from *Burkholderiacepacia* was employed and packed into the packed bed column. The process involved ultrasonic emulsification, which resulted in an increase in production yield from 64% to 68.8%.

VII. RECENT STUDIES IN SUBSTRATES IN BIOFUEL PRODUCTION

1. **Biofuel Production from Novel Prunus Domestica Kernel Oil: Process Optimization Technique:** Prunus domestica, called Ooty Plum, belongs to the family Rosaceae. The kernel part of the seed of this fruit is utilized for the production of biodiesel and showed a promising feedstock for this study. The fuel produced is a cheap, non-edible oil and emerges as a substitute for the diesel which is commercially available. The Plant possesses a large shrub, thorny, and flowers every year in April and the fruit begins to ripe between July and November. Earlier the oil from the kernel of this plant was utilized as a raw material in the larger industries for the production of pharma products such as medicinal supplements, food-based products, and cosmetic products. The plant was cultivated in the Himalayan regions, in the areas of Punjab, and also in the hills of the Nilgiris. This group had chosen a way to valorize the kernel oil of Prunus domestica into an alternative for the fossil fuel-derived diesel and also concentrated on improvising the reaction efficiency and lowering the reactant residues during the process of production of this biodiesel. In addition, this work was conducted to investigate the fuel's compatibility in the operation of diesel engines.

From the plantation fields of Prunus domestica situated in the Nilgiris, Tamil Nadu, India. The reagents used in this process of production include Sodium hydroxide (NaOH), Sulphuric acid (H2SO4), Methanol and Potassium hydroxide (KOH), Hexane (C6H14), and Phenolphthalein indicator. Here, these reagents are involved in the process of evaluation of the end product. The pre-treatment of the kernel oil obtained from Prunus domestica was done by the application of methanol, NaOH, and H2SO4. In this, NaOH and methanol act as a catalyst. Potassium hydroxide is for the determination and evaluation of acid value. Hexane was applied for the removal of impurities.

2. **Experimental Setup and Process Flow:** The experimental setup includes a three-necked- 500ml Round Bottom Flask which was kept in a water bath system. A condenser structure with a double-walled column and for the temperature measurement, a thermometer was installed in two necks of the flask and the neck of the third stage was fitted with a cork made of rubber. A hot plate arrangement with a magnetic stirrer provides the contents with a centripetal acceleration. The extraction process of Kernel oil from *Prunus domestica* was performed by the outer shell removal by the aqueous purification of the kernels of *Prunus domestica* and subsequently, the kernels are allowed to be exposed to sunlight (by insolation) for desiccation (removal of moisture). The extraction of oil from the feedstock was performed using the mechanical expeller, which yields about 0.46 kg of oil extracted from the substrate per kg of the seed that was being utilized. After the extraction of the crude form of the kernel oil, the impurities removed from the oil were achieved by the addition of hexane of 45% (v/v) and heated up to the temperature around 85°C for half an hour at 600rpm. After the heating, the hot oil with impurities was allowed for an hour for the sedimentation of impurities. Then the pure oil on the top was drained by pouring the above liquid with no level of impurities and made free from impurities and hoarded in an air-tight storage facility for further examination of the oil which was extracted. The methyl esters which were named *Prunus domestica* Methyl esters were prepared from the kernel oil. The characterization of this methyl ester was characterized and calibrated with accuracy at a higher standard. These steps are preliminary for the conversion process of the extracted kernel oil to the available commercial bio-diesel. This end biodiesel was matched with the EN14214-European Standards. Then the quality and efficiency of the extracted biodiesel was tested by a series of process by analyzing multiple criteria such as the ratio of the methanol and the oil that was being utilized in the process, experimental duration, concentration of the Sodium hydroxide, and the favorable temperature for the reaction. The above considerations are to be analyzed for the enhancement of PDME and its reaction efficiency. (7) These parameters are listed in the table below.

Table 2: Optimal Conditions for the Yield of Biodiesel from PDKO

Optimal Conditions	Unit	Parameter values
Alcohol to Oil Ratio	-	8:1
Temperature	°C	55
Reaction Time frame	min	120
NaOH Concentration	Weight% (wt. %)	1
Reaction Efficiency of PDME	%	97.89

Table 3: Percentage of influence of Process Variables in the Synthesis of PDME

S. No	Process Parameters	% of influence
1	Alcohol (Methanol)-to-Oil Ratio	51.72
2	Temperature for the reaction	9.50
3	Reaction Time frame	11.2
4	Concentration of NaOH	27.58

3. **Working with Pomegranate Peels as a Novel Substrate:** Pomegranate (Punica granatum), a fruit-bearing shrub belongs to the family Lythraceae. Pomegranate was primarily used in fruit juices, jams, jellies, etc. It acts as a natural exfoliator to remove dead skin cells from your body. The global Market value of Pomegranates was USD 236 million in the year 2021 and was expected to grow 338.6 million USD by the year 2030. These pomegranates are comprised of anti-oxidants and anti-bacterial and anti-cancer activities. In the year 2021, the 1,500,000 was yielded by the global pomegranate market. The pomegranate peels from the fruit contributed about 60% of its weight. These pomegranate peels comprise of reducing sugar and glucose and lignin can be extracted directly with no other prior pre-treatment process. So, this could be a compelling valid reason for nominating it as a substrate for biofuel production by producing lipids. Hence, in this study, the peels of the pomegranates are applied for the production of biodiesel or biofuel by applying a bacterial strain.

4. **Production Process**

- **Strain Selection:** Earlier, the oleaginous bacterial strains such as *Rhodococcus opacus* PD60 were identified that it possesses the capability to accumulate oil up to the volume of 80% of a cell dry weight. The bacterial strains for biofuel production were isolated from the poultry wastes and screened for strains that provide efficient production of lipids and were made purely cultured. The screening process for detecting the strains that possess a good lipid-producing potential was done by staining the strains in a culture (LB Agar) plate by using Sudan Black B Stain. Out of 30 isolates of bacterial strains, only five bacterial strains were selected for the process. Among them, the early or fast-grown strain is selected for the process, based on the optimization studies done on every strain in both pomegranate peels and rice bran powder substrates

- **Process:** This study makes use of two substrates that are Pomegranate peel wastes and rice bran powder. The composition of the production medium encompasses KH2PO4, K2HPO4, sulfates of Magnesium, Manganese, Copper, and Zinc with the presence of water molecules (as hydrates) in their structures and CaCl2 with a quantity of 0.4, 1.6, 0.2, 0.05, 0.001, 0.001 and 0.0005 (all in g/L), which are in correspondence with the above salts. The media was adjusted to the pH level of 4.7 (approx). The production includes the substrate inoculum concentration was fixed at 4% initially. The media were incubated in the Erlenmeyer flask. Then the flask is incubated for the duration of 72 hr at 32°C and the speed of agitation is about 140 rpm. After the process, the reaction mixture was washed 3 to 4 times repeatedly with warm water. The resultant product is added with an equal proportion of ethyl acetate and poured down into a beaker using the separating funnel. FAME was observed in the top phase due to the effect created by the gravitational force. This FAME is termed as Biodiesel derived from renewable sources. (8)

VIII. BIOFUEL PRODUCTION:A VALORIZATION PERSPECTIVE

1. **Corn leaf waste as a Substrate:** The experiment was performed with a waste corn leaf substrate in Jordan. Then the corn leaves from four places (such as China, Jordan, Brazil, and Pakistan) were analyzed for phytochemicals and analogized with one another. The leaf wastes (outer cover) from the corn were treated using the method of pyrolysis at different temperatures by varying the temperatures. As earlier, in phytochemical analysis, the corn leaf waste possesses lignin in the range of 11.9±0.4 and ethanol of composition 13.2±0.2. By performing pyrolysis of biomass (corn leaf waste) under the temperature scaling from 300 to 450 °C. The high conversion yield was observed at 450 °C. The de-volatilization reactions are caused as a result of increasing reaction temperature, which then unexpectedly produces high oil and gas yields. As temperature ranges between 450-650 °C, the liquid fuel yield gets reduced. So it has maintained at the temperature of 450 °C. (9)

2. **Biofuel Production: A Commercial Perspective**

   - **Commercialization of cellulosic biomass from Brazilian Sugarcane Bagasse:** Sugarcane bagasse is promising for the production of biofuel. Then the sugarcane performs a cruel part in Brazil's energy matrix. Almost, all of the energy matrix of Brazil was from renewable energy (which contributes around 44 percent), and 13.5% of the cumulative 44% was only from the source-sugarcane as well. This study emphasizes the production of 2^{nd} generation ethanol and its economic feasibility, the production cost, and retrieval of invested principal amount. In the year 2017, Brazil recorded the 1^{st} Gen Ethanol of 7060 million gallons and the USA reported the amount two times greater than the Ethanol production in Brazil. In addition, India, Thailand, and China produced 280, 395, and 875 million gallons of ethanol respectively.

     As per the economic assessment conducted 1 ton of Sugarcane bagasse results in the production of 231 L of 2^{nd} Gen Ethanol and 300kg of Lignin (in dry weight). Amidst this, the production cost of 1^{st} Gen Ethanol is about 0.56 USD/L and the 2^{nd} Gen is of 1.33 USD/L. From this study, the authors have concluded that the steam explosion of Lignocellulosic Biomass is the most efficient and practically feasible technique that favors the production of bioethanol. Then the study concluded with the efficient production strategies and economic feasibility for 1^{st} Gen and 2^{nd} Gen Ethanol manufacturing. (10)

   - **Comprehensive Policy Analysis Framework for Biofuels:** In the early 1970s, the crisis due to petroleum-based fuels made the people choose an alternative fuel, commonly called Biofuel. In this study, the major biofuel-producing countries are provided with special attention by the policy mechanism created by these countries. Globally, 99% of the global biofuel production was contributed by countries such as India, the USA, Australia, the European Union, Brazil, Canada, Japan, Malaysia and

China. The research examines the biofuel policies of different countries about the production and usage of biofuels. A model called the 'Comprehensive Biofuel Policy Analysis' (CBPA) was created to analyze the composition of biofuel policies. The CBPA framework assesses policy elements to produce a policy rating called the 'Total Policy Measure Support (TPMS)'. This exploration indicates that a higher TPMS score is associated with a more successful biofuel sector, while a lower TPMS score is connected to an underperforming biofuel sector. Additionally, the study uncovers the significance of an equitable policy framework for fostering the upsurge of the biofuel industry. (23)

3. New Generation Biofuel Production:

- **Substrate as Polypropylene Plastic Wastes:** A novel work performed by H Juwono et al., 2019 aims to valorize plastic wastes and waste cooking oil as the prime substrates for the production of biofuels such as biodiesel. Previously, the process of thermal and catalytic cracking of Polypropylene (PP) was the foremost way by which plastic wastes could be efficiently handled. This experiment merges with an idea of the extraction of Liquid Hydrocarbon fuel from the used plastic wastes that are composed of PP, by the process of hydro-catalytic cracking the raw material was catalyzed using Al-MCM-41 mixed with Ceramics that brings about a maximum yield percent of Bio-Gasoline of 93.92. FAME (Fatty Acid Methyl Esters) synthesis by the process of hydro-cracking by the formulated catalyst implemented named (Al-MCM-41), which was taken in the quantity of 11.18 g. This catalyst can be applied more than three times simultaneously. This liquid fuel obtained from these wastes is blended with the commercially used fuels (e.g. Premium fuel of RON numbered 88) and Methyl Tertiary Butyl Ethyl (MTBE) in the proportions of 10:87:5:2.5 for their enhancement in performance which was studied in the Generator Set Engine in accompanied with fuel of gasoline-based. The process ends up with the mixed liquid fuel blend named CB50 variant (CB- Fuel blend), which has the highest range of thermal efficiency at 27.4%, with its corresponding density value of 7,22,550 g/m^3, viscosity of 0.238 cst, flash point of 5.9 °C, and the heating value of 15,46,594 kcal/kg. Also, the study provides us an information that MTBE addition leads to an increased efficiency of CB100 fuel blend over TCB100 by showing the variation of 0.74% and 4.66% to the commercial fuel used at a maximum fuel loading of 2090 Watt. (11)

- **Application of Nanoparticles with Enzymes in Biofuel Production:** Nanotechnology is an extensively emerging field, which is predominantly used in multidisciplinary research studies. This technology works with a principle element (i.e.), nanomaterials (or nanoparticles), in diverse forms of morphology that can applied to the production of products and also in drug delivery in recent days. These nanoparticles can also be applied for the manufacture of these biofuels on an industrial scale. Nano-range systems provide an excellent outcome of the biofuel production process, by immobilizing the enzymes used for the production and also an advantage in the recovery of the enzymes after the bioprocess.

  Nanoparticles mainly prevail in the nano-scale of size fluctuating between the levels from 1 to 100 nanometres (nm). These nanoparticles are primarily synthesized by the physical or chemical modes and nowadays it has been synthesized by green synthesis process using life forms. Nanomaterials manifest beneficial features over the bulk substrates or catalysts used for the production. The ratio of surface area to volume of these particles is high and possesses a tendency to hold high amounts of catalysts thus expressing the large bio-catalytic activity of the enzymes loaded for production. Nanomaterials have overcome many noticeable effects over the enzymatic catalysts used for biofuel processing.

Some of the impacts or demerits overthrown by the application of nanomaterials are, the inactivation of enzymes by organic solvents (such as ethanol, glycerol, etc.), high prices of enzymes, and potential hurdles in the scaling up of production. Immobilization of this enzyme resulted in the efficient downstream separation of enzymes from the processing broth, especially when the magnetic nanoparticles are effortlessly separated.

Immobilization of enzymes such as cellulases and lipases was performed by using nanoparticles such as Fe2O3, Fe3O4, Gold in the form of polymeric form, and silica. Eventually, the magnetic nanoparticles are separated easily. However non-magnetic nanoparticles are a little complex to separate from the reaction mixture. These nanoparticles can be constructed into various forms such as nanotubes, nanofibers, and nanosheets providing an improved ratio of surface area and volume, resulting in the high loading of enzymes, thus involved in the facilitation of reaction and leading to a high bio-catalytic activity

IX. HINDRANCES FOR SUSTAINABLE BIOFUEL PRODUCTION

The major hindrances to the sustainable development of biofuel may be summarized as,

1. Expanding biofuel production might necessitate additional land to ensure sustainability, as biomass production is contingent upon various factors.
2. The cultivation of biofuel feedstocks could place additional stress on water resources.
3. Preserving biomass presents a significant challenge, and the inclusion of storage costs reduces cost competitiveness.
4. Technological advancements in equipment have facilitated cleaner, continuous, and more streamlined production.
5. By-product applications should be categorized.
6. Many processes involve the use of environmentally harmful organic chemicals, posing a challenge for environmentally friendly, high-yield green development.
7. Existing engines are currently not entirely compatible with biofuels, leading to adverse impacts on the stability and durability of these engines. (12)

X. NOVEL APPROACHES TO BIOFUEL PRODUCTION BY CATALYST OR BY IMPROVED CATALYSIS

1. **Improved Catalysis by Ultrasound Waves:** An experiment was conducted for the production of biofuels by the application of novel Fe (III) coupled with Phospho-tungstic acid composites forming a Metal-Organic Framework and ultrasound waves. The catalyst employed in this study was identified as PTA-MIL-53(Fe) and was utilized in generating biodiesel through oleic acid conversion by the process of esterification. This catalyst can

be applied for the production repeatedly five times. The stability of the catalysts used, which was illustrated by the X-ray diffraction Pattern Technology, and the key role played for the stability of the catalyst was performed by the interactions prevailing between the anionic PTAs and the MIL53 (Fe) networks. The study manifested a clear vision of the application of this novel catalyst and the Ultrasound Waves resulted in the production of the biodiesel at an efficient rate. The ultrasound waves generate the evolution of bubbles that get agglomerated leading to the breakdown of biomass.

The process parameters that are considered,

- The quantity of catalysts (ranges from 50-200 mg)
- The duration of the reaction (ranges between 5-20 min)
- The ratios existed between the molar acid ratios: ethanol and n-butanol were 1:4, 1:8, 1:12, 1:16, and 1:20 respectively.
- The power required for ultrasound irradiation ranges from 50-100 watts (W).
- The optimal frequency of the Ultrasound waves generated.
- The optimum percentage of catalysts was utilized.

Table 4: Optimal Values for the Process of Production:

Process Parameters	Unit	Optimal Values
Amount of Catalyst	mg	150
Time Duration	min	15
Molar acid Ratio: (ethanol or n-butanol)	-	1:16
Output Power Required	watt (W)	100
Optimum Frequency of Ultrasound Waves	hertz (Hz)	35
Optimum % of Catalyst	%	30

These are the optimal values for process variables required in this process for a high yield of biodiesel from the biomass supplied. (13)

2. **Lime with Na3PO4 – An Effective Catalysts for the Production:** This work was performed as a comparative analysis of biofuel synthesis by using various catalysts such as Sodium hydroxide, Calcium oxide (Lime), Sodium orthophosphate, and also with Potassium hydroxide and found the effective catalysts from the used ones. CaO and Na_3PO_4 showed a high glycerine obtained when compared to NaOH and KOH. The results proved that the yield percentage of heterogeneous catalysts is higher than that of homogeneous catalysts. The densities of the produced biofuel are almost corresponding to the present biofuels that are commercially utilized in our day-to-day life. The properties of these biofuels are higher than the diesel which was used conventionally. Hence, these biodiesels can be blended with fossil fuel-based diesel to achieve suitable proportions in the specification range of CI engines. (14).In contrast, the synthesis of a specific biofuel from dairy scum oil employed the use of sodium phosphate as a catalyst. Initially, sodium phosphate was synthesized in the form of rod-shaped structures during the glycerol

purification process, resulting in catalyst particles ranging from 2 to 100 µm in size. Through a transesterification reaction, the biodiesel was produced with an impressive yield of 97.7%, utilizing a catalyst concentration of 4%. (15).Subsequently, the CaO derived from hydrated lime was employed in the process of biofuel production. This investigation also sheds light on the influence of moisture or water content in the reaction mixture. When the reaction mixture exhibits elevated moisture levels, the catalyst undergoes conversion into Ca(OH)2, resulting in a decline in FAME production. Conversely, maintaining the water content at or below 5% resulted in a notable increase in the yield, reaching an impressive 97.2%. (16). Conversely, within a distillation column featuring two distinct reactive segments, one section is filled with Amberlyst-15, a polymeric acidic catalyst, while the other is packed with either CaO or Al2O3, all with the aim of enhancing the biodiesel yield, specifically in the form of FAME. (17). Additionally, calcium oxide (CaO) found an innovative application in the production of the targeted biofuel. In this novel approach, powdered lime (CaO) was combined with 5% zinc concentration and subjected to calcination at a temperature of 900°C. Subsequently, this meticulously prepared catalyst was employed in the biofuel production process. (18)

3. **A MTV (Multivariate)-UiO-66 Catalysts-In the Biofuel Synthesis:** This research presents the utilization of a complex catalyst- Multivariate-UiO-66 structures (where UiO-66 is an archetypal metal-organic framework) for the synthesis of butyl butyrate. Alongside the structures of an individual component, a mixed-linker system comprised of multiple chemical compounds was utilized to create: the catalytic complex MTV-UiO-66(COOH)2, which was then incorporated with terephthalic acid which was marked as component-A and with another component 1, 2, 4, 5-benzene tetracarboxylic acid which is marked as B, and the complex MTV-UiO-66(OH)2, which comprises terephthalic acid along with another new component-C which is 2,5-Dihydroxyterephthalic acid in various proportions, resulting in nine structures in total. Comprehensive characterization of the structures reveals the successful and uniform integration of functionalized linkers enclosed inside the MOF (Metal-Organic Frameworks) crystals, facilitated by an important and appreciable level of cluster defects due to the synthesis conditions. While the parameters such as surface area and total volume of the pore, the resultant values decrease with the functionalized linkers incorporated at higher levels, these values remain slightly reduced than the molar ratios of initial values, as denoted by the 1H- Nuclear Magnetic Resonance interpretations. Among the two systems, MTV-UiO-66 structures containing 75% of the functionalized linkers and then the percentage yield BDC was 25% demonstrate an optimal function, achieving 92% and 89% of the conversion rates for butyl butyrate using MOF (UiO-66) in the ratio 1 of A: 3 of C and the MOF (UiO-66) in the ratio 1 of A: 3 of B and respectively, with just 1 weight% of the loaded catalyst. This accomplishment exceeds the outcomes of significantly flawed single-component functionalized structures, even though it used twice the catalyst loaded, thus highlighting the effectiveness of the multifaceted approach in improving catalytic performance. Success from the employment of this method had attributed to the heightened density of active sites via partial modification, alongside sustaining the greater surface area and volume of the pores compared to solely altered structures for the use, which promotes improved entry to these locations. Nonetheless, not entire multivariate-MOF frameworks exhibit superior performance to their single-linker counterparts, owing to the mixture of these factors associated with the active site concentration and internal diffusion limitations. This underscores the critical role of MOFs' characteristics in dictating their catalytic performance, leading to the creation of a model working based on linear

regression by these attributes. By calculating weights assigned to each characteristic, the model is fine-tuned to align with the information gathered from the conducted experiment that utilized the UiO-66-derived catalysts in our butyl butyrate production studies. Results indicate that active site density, indicated by the flaws or the functional groups on the linker, exerts greater influence than the surface area and then the levels of catalyst loaded, and both have a similar influence on the prediction of conversion according to the model's results. These intriguing discoveries open avenues for the positive progress of exceptionally efficient UiO-66-type derived catalysts in the production experiments of biofuels. (15)

4. **HCA-Immobilized AuNPs Amine Grafted SBA-15 Named Catalyst in Production of Biofuels:** The optimal biodiesel production yield from animal fat was attained by controlling different factors such as the molar ratio, the quantity of the formulated catalyst which possesses AuNPs (Gold Nanoparticles) immobilized in the HCA (Human Carbonic Anhydrase) which was accompanied by the Santa Barbara Amophous-15 (which is a Mesoporous Silica) grafted by amine was added, reaction duration, the method employed, and temperature settings. The synthesis operation commenced with the extraction of fat from the biomass used, followed by treating the derived fats through glycerolysis. Glycerolysis involved combining oil with glycerol at a ratio of 2.5 g/grams of oil mixed, then the mixture was heated up to the temperature of 110°C which was performed for 90 minutes. Biofuel synthesis utilized transesterification of the substrate used (which is the animal fat) with a molar ratio of 1:3 which was operated at the process temperature of 60°C and with 350 rpm speed for 60 minutes or an hour. Analysis was performed by the analytical instrumentations that are Fourier Transform Infra-Red Spectroscopy and Gas Chromatography-Mass Spectroscopy, these confirmed the existence of fatty acids in the substrate and its conversion into methyl ester form of the fatty acids utilized. This process achieved a yield percentage of 94%, and further investigation into the performance of the biofuel produced when applied and the complete physical-chemical properties of the resultant biofuels will be conducted to characterize cum enhance this resultant biodiesel for future endeavors. (16)

5. **A Catalytic Activity of Unbound *Candida Antarctica* Lipase-A in Biofuel Processing:** An environment-friendly technique for creating biodiesel was successfully developed through the utilization of FPO, a free fatty acid (FFA)-rich waste frying oil as the raw material and equipped along with an innovative catalyst, the free liquid phase lipase-A enzyme (CAL-A) derived from the *Candida Antarctica*. The outcomes indicated that the free or unbound CAL-A exhibited remarkable resistance to methanol and could be employed to produce biodiesel through a methanol addition process in a single-step mode. Furthermore, the free Lipase-A demonstrated the capability to concurrently catalyze the transesterification reaction that processes the Frying Palm Oil and the esterification reaction for the conversion of unbound FFA in generating biodiesel even in the presence of enormous contents of water available. Through response surface methodology (RSM) optimization, the following reaction conditions were identified as optimal: 16.6 of the water content in weight and then the loaded lipase level of 5.5 in weight, maintained at 30 °C for 22 hours. The impact created by the variables that are associated with the reaction was observed to decrease in the sequence (water content > time duration of the reaction > the loaded lipase). The calculated energy of activation (Ea) for producing the required biodiesel stood at the final output of 32.96 in the unit kJ/mol, with kinetic parameters like K'm and also the parameter Vmax being 0.675 moles/L and

0.0238 moles/L min correspondingly. This research introduces an environmentally sound approach for manufacturing biodiesel by utilizing waste frying oil containing increased levels of water and unbound fatty acids as the source material, in conjunction with an economical free liquid lipase as the catalyst (17).Likewise, lipase enzymes sourced from organisms such as Carica papaya (the Papaya plant) and Rhizopusoryzae (a filamentous microfungus) find application in the production of the targeted biofuel. The lipase derived from Carica papaya exhibits an inherent propensity for self-immobilization, while the lipase extracted from Rhizopusoryzae is immobilized through a matrix solution composed of Sodium alginate (a natural polysaccharide) and Polyvinyl alcohol (a synthetic polymer material). These two catalysts are employed to achieve a remarkable biodiesel yield in the form of FAME (Fatty Acid Methyl Esters) (18),(19). Furthermore, lipase obtained from the Penicillium expansum species was subjected to cross-linking immobilization and applied to achieve an impressive 85.7% conversion rate of microalgae oil into biodiesel. Subsequently, lipase derived from the thermophilic fungus known as Thermomyces lanuginosus was immobilized within mesoporous silica matrices, which were employed to facilitate production in nanoparticle form.

XI. A FRESH CATALYST FROM THE REPURPOSED WASTE GLASSWARE AND EGGSHELLS

A distinctive methodology (29), was employed to successfully create a new catalyst. The catalyst precursor such as lime in combination with SiO2 was formed using discarded laboratory glass which comprises SiO2 in its structure, and from the discarded eggshells the lime was obtained. This combination was further enhanced along with the incorporation of the compound Cerium oxide to generate the innovative complex of catalyst that comprises Cerium-Calcium oxide (lime)-Silicon dioxide. Thorough characterization unveiled the summary that, the resulting catalyst owes the entire necessary attributes for the efficient production of bio-diesel. An extensive analysis of parameters was conducted, demonstrating the catalyst's efficacy. The optimal configuration of independent factors consisted of a process temperature is about 70°C, a duration of 100 min, a molar ratio of the methanol-to-oil is 11, and the amount of catalyst that was loaded is about 3% in weight. This configuration yielded a biodiesel output of 95.29 wt. %. Moreover, an examination of catalyst reusability indicated that the catalysts used can surely be employed for five iterations of the process without experiencing a notable reduction in the activity of those catalysts, affirming their viability for practical use. In conclusion, the synthesized catalyst exhibits remarkable efficiency and holds promise for biodiesel manufacturing.

1. **Bismuth Silicate-A Novel Catalyst for Biofuel Production:** The study was involved in the novel application of Bismuth Silicate (such as Bi4Si3O12 and Bi2SiO5) based catalysts of three different forms, which are named B10, B30, and B40. Among these, B30 was noted for its higher efficiency in producing biodiesel. This study was similar to that of the PTA-MIL53 (Fe). This method revealed that an increase in the total acidity, surface area, band gap energies, and volume of the pores was caused by to action of Ultrasound waves, which in turn reduced the time by about 30 minutes. It was observed at the B30 catalyst was identified that the trans-esterification reaction was 90% high at optimal conditions. The catalyst also possesses 80% catalytic activity even after five repeats (30).

2. **Extraction Methodologies applied in Biofuel production:** The extraction methods applied vary from different feedstocks fed to a reactor aiming for the production of biofuels. Some of the methods of extraction applied for the biofuel products from the different generation biomass are Conventional Solvent Extraction (CSE) for the first-generation feedstocks such as energy crops. Mechanical methods such as CSE, Supercritical Fluid Extraction (SFE), expeller and oil press, Physical Support Solvent Extraction Method (PSSE), and other innovative techniques can be applied for second-generation feedstocks and the biofuels from third-generation feedstocks can be extracted by applying the techniques that are being applied for the first generation biofuels production that includes Supercritical Fluid, Conventional Solvent and PSS Extraction methods. (31) A Novel method applied to extract the biofuel from the feed is Switchable solvent extraction as well. Fig 3 shows the Production Process of Biofuels-Flow Diagram

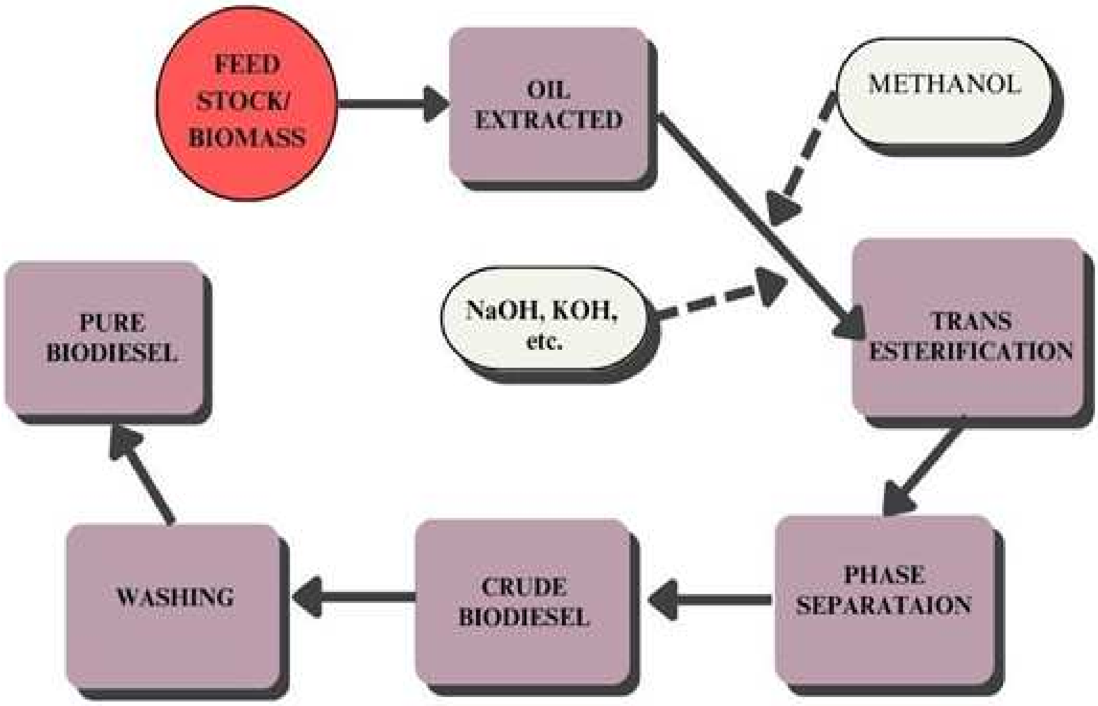

Figure 3: Production Process of Biofuels-Flow Diagram

3. **Biofuel Performance: Parameters for Analysis:** For the analysis of biofuel performance, the primary process is to contemplate and deduce the information on the indicators of biofuel performance. The indicators such as analysis of the flow patterns of heat, power loss due to the friction between the piston and the cylinder walls (Friction Power), brake-specific energy consumption, and emission levels of smoke are the parameters selected for their significance in fuel operation in diesel engines (29). These can be represented as in Fig 4.

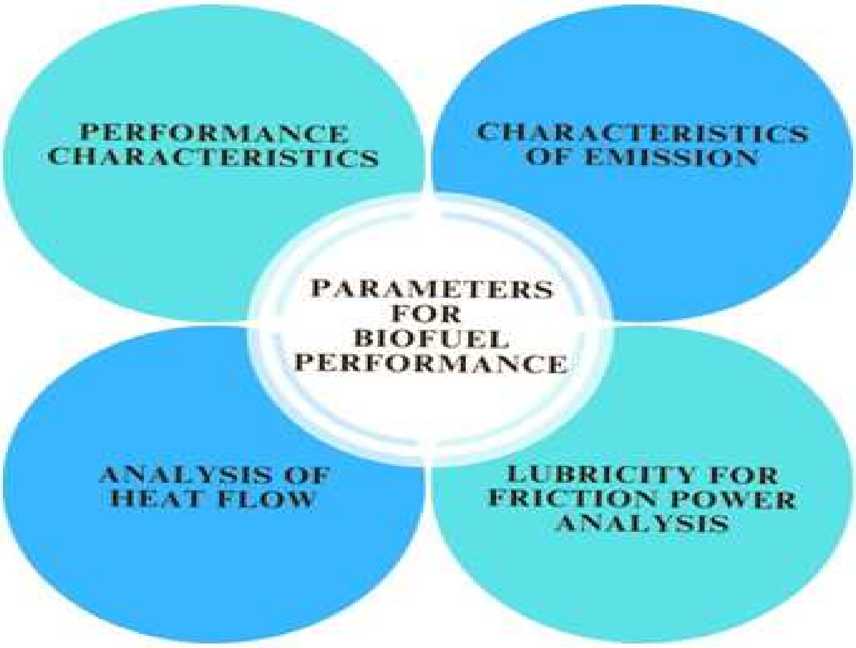

Figure 4: Evaluation Parameters for Biofuel Performances

The emission parameters such as gases exempted from the emission of the engine should be screened for unburnt hydrocarbons, CO gas, Nitrogen oxide gas, and smoke particles, under the emission characteristics parameter. Then the performance was analyzed by Brake Thermal Efficiency (BTE), Mechanical and volumetric efficiency, Brake Specific Energy Consumption (BSEC), Air-Fuel Ratio, Brake Specific Fuel Consumption (BSFC), and Exhaust Gas Temperature. Analysis of heat flow can be done by monitoring the Heat utilized by Brake power, and Heat lost via radiation, cooling system equipped with cooling jackets, and exhaust gas. (31)

XII. BIOFUEL: FUTURISTIC PROSPECTS

Small-scale bio-refineries integrated along with the farms similar to the setup of DWC (6) can be developed and the biofuel be produced and utilized for domestic purposes. The substrates with high lignocellulosic content can be applied for the production of conventional biofuels. Food waste from the result of municipal waste management processes can be the next view. Novel catalysts which are synthesized from either green or chemical methods, can be applied for the improvements in the yield of biofuels. Lab-scale reactors, as explained in (5) and (6), can be scaled and applied at pilot and industrial levels of production. Enzyme immobilization using nanoparticles can contribute to higher conversion. Biofuels blended with conventional fuels can be encouraged. Then the efficiency of biofuel needs to be increased as well to meet the daily needs of the people, which in turn to be used as fuel for routine by bypassing the utilization of fossil-derived fuels. By applying emerging fields such as systems biology and computational biology, the microbial strains utilized for biofuel production are improved by the strain improvement process which includes genome editing and engineering. As an illustration of advanced scientific approaches, computational biology can be harnessed to create models of biomass and subsequently employ them in the analysis of strategies for optimizing biofuel production. To illustrate, a model centered on

Cyanobacteria was developed, and a meticulous screening of specific metabolic pathways was conducted to assess their viability for efficient biofuel generation. The chosen Cyanobacterial strain for this investigation was Synechocystis sp. PCC 6803. (32)The novel and modern approach of process optimization can be done by applying Machine learning by feeding the process variables and their corresponding values for the production process of biofuels. The strategy of early prediction was employed in a research endeavorcentered only on Spirulina platensis, an organism. This investigation brought to light the advantages of early prediction in determining both biomass and biodiesel yields. These mathematical models can also serve the purpose of forecasting the optimal conditions necessary for the biomass to produce the desired outcome. It's worth noting that the success of this study hinges upon the availability of accurate and appropriately formatted datasets.(33)

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