**Biofuel - Process, Novel Approaches, Future Perspectives**

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**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, natural gas) at a high rate. This leads to the diminution of natural resources, in addition to the statement, an enhanced levels of Green House Gases in the atmosphere yielding Global Warming. To alleviate these such 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 a 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 about the biofuels, sources, and case studies in the production of biofuels or explains the recent approaches such as optimizing the production, utilizing novel substrates, modifications made in the bioreactor design for the improvements in the yield. This chapter had also included with novel catalysts used for the production process and also comprises of techniques for the extraction of biofuels from reaction mixture in 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 the improving the efficiency of biofuel production was explained in this chapter.

**1.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 out from various biomass sources or from any other biological substances. Countries such as North American, European and Southeast-Asian countries are working on the large-scale manufacturing of these biofuels from the life sources. As reported in the survey by the year 2022, the top ten countries that steer them to indulge in the biofuel production frequently are known to be USA, India, China, Brazil, Malaysia, Italy, 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 of technology 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 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 had helped us to overthrow the extents of the fossil fuels-based society. Biofuel plays an important role in decarbonizing the environment and the global temperature was decremented to 2°C by the reduction in the amount of Green House gases to the level ~43%. In the study of R. Zah *et al*, 2009, (3) had concluded the ways to ameliorate the biofuel sustainability. The scientists have developed an evaluation of the biofuels and their environmental aftermaths. Also disclosed about 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 linked with various trade activities. The impacts are multifaceted and heavily influenced by policy measures. Consequently, assessing the comprehensive global effects of biofuel trading on the environment and economy remains challenging. However, from the collective findings of this issue, some conclusions can be drawn to mitigate negative impacts and harness the positive potential of future biofuel use.

- Policy measures play a pivotal role in driving biofuel production and utilization. However, the outcomes of these policies vary significantly based on global market conditions and the interactions with other policies.

- Biofuel production is closely intertwined with the global market for food and feed commodities. This connection arises from competition for agricultural land, primarily for reasons beyond feedstock. To ensure sustainability, future biofuel production should minimize competition for land and rely more on residual materials.

- Smaller bioenergy projects generally offer environmental and social benefits with relatively low risks. Conversely, larger-scale projects tend to carry greater economic risks, and their social benefits might be less positive.

- 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.

**2.Biofuel- Global Market**

After Post COVID-19 Pandemic and Ukraine- Russia War, in the year 2022, the biofuel production faced the crisis of downfall in the supply levels of 1st generation feedstock supply, as Russia plays a crucial role in the supply of 1st generation feed stocks 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 had contributed in the reduction of carbon emissions, Green House Gas emissions, Global temperature, and had inculcated a culture of utilizing the agro and food wastes, valorization of resultants of certain bioprocessed by-products from the industries globally. (4) Figure 1 depicts the diagram representation of Global Biofuel market.

**Fig 1: Pie Diagram Representation for Global Biofuel Market**

**3. Sources of Biofuels:**

Primarily, the biofuels are produced from the biomass sources or by-products of various plant sources that were the residues of the agricultural activities. The sources are forest residues (such as firewood, 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 the biofuel production. The starch present in the sugarcane stems and beets, for the oils present in the seeds of sunflower, rapeseed and soybeans are being fermented for the bio-alcohol and bioethanol manufacturing. The crops chosen and are to be plenteous in sugars, starch and oils. Then the plant sources such as silver grass (*Miscanthus sinensis*), Nettlespurges (Jatropha *curcas*), Elephant grass, switchgrass, Cassava (*Manihot esculenta*), 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 yields 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 the biofuel production, the sources are sorted under two titles namely Primary and secondary biofuels. In addition to the secondary class of biofuel are further sub-categorized into three classes namely, first, second and third generation sources. Correspondingly, the biofuel products from these sources or substrates can termed as first, second and third generation biofuels as well. Now new generation biofuels are produced from plastic wastes. The research is in still progress to generate the biofuels in industrial scale at very high volumes (2).

**4. Biofuels- Classification:**

The categorization of biofuels is done on the basis of 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,



**Fig 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 Switch grass, 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 BIOFUELSThese 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. |

**5. Process Steps involved in Biofuel Production: A Flow Representation:**

The biofuel production process involved in 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 proceeded with further processing steps to undertaken for the production of desired biofuels. For that, initially the biomass is treated by undergoing processes such as thermo-chemical process and bio-chemical conversions (Fig 3).

The thermos-chemical process includes the methods such as pyrolysis, gasification, liquefaction and, the bio-chemical conversion took place by the application of methods of such as anaerobic digestion and fermentation. Pyrolysis is an anaerobic process that in breakdown of long fatty acid chains by the application of heat at very high temperature scales. Pyrolysis can be classified as fast and slow pyrolysis. Here, 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 biomass to result in energy-rich gaseous products or fuels. Liquefaction involved in the conversion of provided biomass into liquid hydrocarbons of high stability under low temperatures and high pressures.



**Fig 3: Methods applied for Biomass Processing**

**6.Case Studies: Novel Approaches in Biofuel**

**6.1 Novel Bioreactor System in Biofuel production:**

**6.1.1 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 the biofuel from the soybean oil was used as a chief substrate. The reactor showed a result of high efficiency mixing, higher rate of conversion of the substrates (soybean oil) into the biofuel and an excellent mass and heat transfer attributes are noticed. 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 have a tendency to enhance the agitation of the fluid at a higher rate. The functioning of this system had 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 was first designed and analyzed under the method of dynamic simulation by mathematical and physical model. Later the reactor was built experimentally and noted.

**6.1.2 Materials Involved:**

The prime source of the biochemical reaction which is needed to be converted is Soybean Oil, which was first procured from the Meryer Chemical Technology Company situated at Shanghai, China. The soybean oil possesses a composition of various fatty acids which includes Palmitic, Oleic, Linolenic and Stearic. In the addition to the soybean oil, the materials included in the composition of the feed stock, 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.

**6.1.3 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, involve in the significant improvements in the performance of the mixing. For furthermore clarification of the intermixing of the fluids inside the reactor and the reactor wall deformation are calculated by the Three- dimensional modules of Simulation process for the reactor was carried out by the system software named ANSYS Platform. Here the simulation the calculating Solid domain was carried out by the Mechanical and the fluid domain simulation is carried out by the Fluent and then the System Coupling Module works 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 was 10 and 4 mm respectively. An interface system, System Coupling Module works by the methodology of Separate Solution Method, helped to calculate the domains of fluid and solid in a discrete manner at a disparate time intervals. The results are converged for the final output.

**6.1.4 Dividing Wall Column (DWC) Technology in the Production of Biofuels:**

Distillation plays a prime role, since from the beginning of the biofuel production, for the extraction of biofuel from the processed feedstock. It was a furtherance in the production process that promotes favorable conditions to upswing 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 comprises of techniques such as azeotropic distillation, reactive distillation and extractive distillations by constructing the DWC in terms of DWC, R-DWC, A-DWC, E-DWC respectively. These columns are exploited to work for the tasks for the processes including the FAME (Fatty Acid Methyl Esters) and DME (Dimethyl Ether) synthesis using the R-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.

**6.1.5 Reactor- Experimental Setup and Working**

**6.1.6 Peristaltic Reactor: Construction& Working**

The reactor system was equipped with 3-6 identical segments of peristaltic tube of similar dimensions. These tubes are soft, flexible made of materials such as rubber which has easy deforming tendency and are capable of creating the phenomenon peristalsis. Every peristaltic segments of the reaction system possess an elastic peristaltic tube, a fixed rigid tube, a holding stand with 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 of 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 feed stock, a central controlling system, a peristaltic pump and a pressure regulator unit. Using the peristaltic pump, the feed stock containing soybean oil is pumped out from the storage tank to the reactor with the help of the pulsating pressure created by the pump. This made the sections of the peristaltic pump to expand and contract in a periodical way enabling the substrate mixing at a higher rate. The system for temperature control comprises of a thin heating element in the structure of a film and a temperature control unit, which checks out and regulate the temperature favorable for the reaction inside the reactor, which can help to attain high rate of conversion. The pressure controlling or regulating device which was placed at the outlet had involved in bringing the peristaltic amplitude to a desired size and also assist the variation of the peristaltic period by the adjustment of the pulsating pressure cycle.

**6.1.7 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 which was fastened to an air-bath or shaker bath system. An incubator is equipped with the rigid tube reactor and the 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 had showed a high rate of conversion.

**6.1.8 Dividing Wall Column: Working**

The DWC unit was actually 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 comprising mid-boiling constituent, 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 a same unit and resulted in the minimal temperature difference in between two walls, it provides a clear view on the accomplishable implementation with a minimal heat transfer and an insignificant effect on the performance of the column. This experimentation elaborates about the role of this DWC in industrial production of biofuel. This novel construct is capable of decrementing the capital invested and minimize the energy requirements up to 17%. By performing methanol and glycerol recovery in the same reaction unit had conserved 27% of the energy utilized. 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 operations 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 |
| Material used for the Wall | - | Stainless Steel | Rubber |
| Viscosity of the Fluid (Feed stock) | m.Pa.s | 1 to 400 | 1 to 400 |
| Poisson’s Ratio | - | - | 0.47 |
| Young’s Modulus  | Pa | - | 3 x 10^6 |

**7 Recent Studies in Substrates in Biofuel Production:**

**7.1 Biofuel production from novel Prunus domestica kernel oil: process optimization technique**

Prunus domestica, called as 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 an alternative fuel for available diesel fuel. The morphology of this plant is large shrub, thorny and flowers at every year of April and the fruit begins to ripe between the months of July and November. Earlier the oil from the kernel of this plant was used in the pharmaceutical industries for the production of medicines, cosmetics and food products. The plant was cultivated in the Himalayas, Punjab and the Nilgiris. The group had chosen the way to valorize the kernel oil of Prunus domestica into an alternate 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 includes 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. For 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.

**7.2 Experimental Setup and Process Flow**

The experimental setup includes a three necked- 500ml Round Bottom Flask which was kept in a copper water bath. A double-walled condenser and a thermometer was installed in two necks of the flask and the third neck is fitted with rubber cork. A hot plate arrangement with 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 expose to sun light (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/ kg of seed. After the extraction of kernel oil in a crude form, the impurities are removed from the oil was 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 decanted and made free from impurities and stored in an air-tight container storage for the analysis process. The methyl esters which were named as *Prunus domestica* Methyl esters was prepared from the kernel oil. The characterization of this methyl ester was characterized and calibrated with accuracy in higher standard. These steps are preliminary for the conversion of kernel oil into a conventional biodiesel. This end biodiesel was matched with the EN14214-European Standards. Then the quality and efficiency of the extracted biodiesel was tested by the series of process by analyzing the parameters such as the alcohol (methanol) to oil ratio, experimental duration, reaction temperature, concentration of NaOH. 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 | deg C | 55 |
| Reaction Time frame | Min | 120 |
| NaOH Concentration | 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 |

**7.3 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. Global Market value of Pomegranate was USD 236 million in the year 2021 and was expected to grow 338.6 million USD by the year of 2030. These pomegranates comprises of anti-oxidants, 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 were 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.

**7.3.1 Production Process**

**7.3.1.1 Strain Selection**

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

**7.3.1.2 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, MgSO4.7H2O, MnSO4.H2O, CuSO4.5H2O, ZnSO4.7H2O and CaCl2 with a quantity of 0.4, 1.6, 0.2, 0.05, 0.001, 0.001 and 0.0005 (all in grams per litre) respectively. The pH of the media was adjusted approximately to 4.7. The production includes the substrate inoculum concentration was fixed to the 4% initially. The media were incubated in the Erlenmeyer flask. Then the flask is incubated for the duration of 72hrs at 32°C and the speed of agitation is about 140 rpm. After the process, the reaction mixture was washed with warm water for 3 to 4 times. The resultant product is added with equal proportion of ethyl acetate and poured into a separating funnel. By the influence of gravitational force, the FAME formed on the top of the mixture. This FAME is termed as Biodiesel derived from renewable sources. (8)

**8 Biofuel Production:** **A Valorization Perspective**

**8.1 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. In this study, the corn leaf waste biomass was treated by the method pyrolysis at different temperatures by varying the temperatures. As earlier, in phytochemical analysis, the corn leaf waste possess 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 degree C. The high conversion yield was observed at 450 deg C. The devolatilization reactions caused as a result of increasing reaction temperature, which then unexpectedly produce high oil and gas yields. As temperature ranges between 450-650 deg C, the liquid fuel yield gets reduced. So it has maintained in the temperature of 450 deg C. (9)

**8.2 Biofuel Production: A Commercial Perspective**

**8.2.1 Commercialization of cellulosic biomass from Brazilian Sugarcane Bagasse:**

Sugarcane bagasse is promising for the production of biofuel. Then the sugarcane plays a cruel role in Brazil's energy matrix. Almost 44% of the energy matrix of Brazil is from renewable energy and around 13.5% is from only the sugarcane. This study emphasizes about the production of 2nd generation ethanol and their economic feasibility, the production cost, retrieval of invested principle amount. Year 2017, Brazil records the 1st Gen Ethanol of 7060 million gallons and the USA had reported with the amount two times greater than the Ethanol production than the Brazil. In addition, India, Thailand, China had produced 280, 395, 875 million gallons of ethanol respectively.

As per the economic assessment conducted 1 ton of Sugarcane bagasse results in the production of 231 litres of 2nd Gen Ethanol and 300kg of Lignin (in dry weight). Amidst this the production cost of 1st Gen Ethanol is about 0.56 USD per L and the 2nd Gen is of 1.33USD per 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 bioethanol. Then the study concluded with the efficient production strategies and economic feasibility for 1st Gen and 2nd Gen Ethanol manufacturing. (10)

**8.2.2 Comprehensive Policy Analysis Framework for Biofuels:**

In the early 1970s, the crisis due to petroleum-based fuels made the people to choose an alternative fuel, commonly called as 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 the countries such as India, USA, Australia, European Union, Brazil, Canada, Japan, Malaysia and China.The research examines the biofuel policies of different countries in relation to the production and usage of biofuels. A model called the 'Comprehensive Biofuel Policy Analysis' (CBPA) was created to analyse the composition of biofuel policies. The CBPA framework assesses policy elements to produce a policy score called the 'Total Policy Measure Support (TPMS)'. The research 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 importance of a well-balanced policy framework for the development of the biofuel sector. (23)

**8.3 New Generation Biofuel Production**

**8.3.1 Substrate as Polypropylene Plastic Wastes:**

A novel work was performed by H Juwono et al., 2019 aims to valorize the plastic wastes and the waste cooking oil as the prime substrates or raw materials for the production of biofuel production such as biodiesel. Previously, by the process of thermal and catalytic cracking of Polypropylene (PP) is the foremost way by which plastic wastes can 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 catalytic hydro-cracking by the application of the catalyst 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 are blended with the commercially used fuels (for e.g. Premium RON 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 as 27.4%, with its corresponding density value 722.55kg per m3, viscosity of 0.238 cst, flash point of 5.9 degree C, and the heating value of 15,465,94 kcal per 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)

**8.3.2 Application of Nanoparticles with Enzymes in Biofuel Production:**

Nano technology, 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 recent days. These nanoparticles can also be applied for the production of biofuels in a large-scale manufacturing. These nano-range systems provide an excellent outcome of 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 prevails 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 manifests beneficial features over the bulk substrates or catalysts used for the production. The ratio of surface area to volume that these particles are high, and possess a tendency to hold high amounts of catalysts thus expressing the large bio-catalytic activity of the enzymes loaded for the productions. Nanomaterials had overcame many noticeable effects over the enzymatic catalysts used for the biofuel processing.

Some of the impacts or demerits overthrown by the application of nanomaterials are, inactivation of enzymes by organic solvents (such as ethanol, glycerol, etc.), high prices of enzymes, potential hurdles in the scaling up of production. Immobilization of these enzyme resulted in the efficient downstream separation of enzymes from the processing broth, especially 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 in an easy manner. But non-magnetic nanoparticles are little complex to separate from the reaction mixture. These nanoparticles can be constructed into various forms such as nanotubes, nanofibers, nanosheets provides a high surface area to volume ratio, which can lead to high loading of enzymes, thus involved in the facilitation of reaction and led to a high bio-catalytic activity

**9 Hindrances for Sustainable Biofuel Production**

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

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

**10 Novel Approaches on Biofuel Production by Catalyst or by Improved Catalysis**

**10.1 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. This catalyst used was pronounced to be PTA-MIL-53(Fe), which was applied for the production of Biodiesel by the conversion of Oleic Acid by the process of esterification. This catalyst can be applied for the production repeatedly for five times. The stability of the catalyst 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 on the application of this novel catalyst and the Ultrasound Waves had resulted in the production of the biodiesel at an efficient rate. The ultrasound waves generate the evolution of bubbles gets agglomerated leading to the breakdown of biomass.

The process parameters that are considered,

* The quantity of catalysts (ranges from 50-200mg)
* The duration of the reaction (ranges between 5-20 mins)
* 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 used 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 | Watts(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)

**10.2 Use of CaO and Na3PO4 Catalysts for the production:**

This work was performed using various catalysts such as NaOH, KOH, CaO and Na3PO4 for the production of biodiesel. CaO and Na3PO4 showed a high glycerine obtained when compared to NaOH and KOH. The results proved that the yield percentage of heterogeneous catalysts is higher than the homogeneous catalysts. The densities of the produced biofuel is almost similar to that of the conventional biofuels. The fuel properties of these biofuels are higher in comparison with the diesel that is used conventionally. Hence, these biodiesels can be blended with the fossil fuel-based diesel to achieve suitable proportions in the specification range of CI engine. (14)

**10.3 Use of MTV-UiO-66 based Catalysts:**

This research presents the utilization of MTV-UiO-66 structures as catalysts for the synthesis of butyl butyrate. Alongside individual component structures, two mixed-linker systems are created: MTV-UiO-66(COOH)2, incorporating terephthalic acid (A) and 1, 2, 4, 5-benzenetetracarboxylic acid (B), and MTV-UiO-66(OH)2, which includes terephthalic acid (A) and 2,5-Dihydroxyterephthalic acid (C) in various ratios, resulting in nine structures in total. Comprehensive characterization of the structures reveals the successful and uniform integration of functionalized linkers within the MOF crystals, facilitated by a significant level of cluster defects due to modulation synthesis conditions. While the surface area and pore volume values decrease with higher incorporation of functionalized linkers, these values remain slightly lower than the initial molar ratio, as indicated by 1H NMR findings. Among both systems, MTV-UiO-66 structures containing 75% functionalized linkers and 25% BDC demonstrate optimal performance, achieving 89% and 92% conversion rates for butyl butyrate using UiO-66(1A:3B) and UiO-66(1A:3C) respectively, with just 1 wt.% catalyst loading. This achievement surpasses the results of highly defective single-component functionalized structures with double the catalyst loading, underscoring the success of the multivariate approach in enhancing catalytic activity. This success is attributed to the heightened density of active sites via partial functionalization, alongside maintaining greater surface areas and pore volumes compared to solely functionalized structures, which promotes improved access to these sites. Nonetheless, not all MTV-MOFs exhibit superior performance to their single-linker counterparts, owing to a combination of factors related to active site density and internal diffusion limitations. This underscores the critical role of MOFs' characteristics in dictating their catalytic performance, leading to the creation of a weighted linear regression model based on these attributes. By calculating weights assigned to each characteristic, the model is fine-tuned to align with experimental data from the 33 UiO-66-based catalysts developed in our butyl butyrate production studies. Results indicate that active site density, indicated by defects or functional groups on the linker, exerts a relatively greater influence than surface area and catalyst loading levels, both of which exert a comparable impact on conversion prediction based on the model's outcomes. These intriguing discoveries open avenues for the development of highly efficient UiO-66-based catalysts in biofuel production studies. (15)

**10.4 Use of Catalyst HCA Immobilized AuNPs Amine Grafted SBA-15 in Biofuel Production:**

The optimal biodiesel production yield from animal fat was attained by controlling different factors such as the molar ratio, the quantity of HCA (Human Carbonic Anhydrase) Immobilized AuNPs (Gold Nanoparticles) amine grafted SBA-15 catalyst added, reaction duration, method employed, and temperature settings. The process of biodiesel synthesis commenced with fat extraction, followed by treating the fats through glycerolysis. Glycerolysis involved combining oil and glycerol at a 2.5 g/g oil ratio, heated to 110°C for 90 minutes. Biodiesel synthesis utilized transesterification on animal fat with a molar ratio of 1:3, a catalyst concentration of 0.5%, operating at 60°C and 350 rpm for 60 minutes. Analysis using FTIR and GC-MS spectroscopy confirmed the presence of fatty acids in animal fat and their conversion into Fatty Acid Methyl Ester. This process achieved a 94% yield, and further investigation into physiochemical properties and performance will be conducted to characterize and enhance the biodiesel for future endeavours. (16)

**10.5 Free *Candida antarctica* Lipase-A (CALA): A Novel Catalyst:**

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 free liquid lipase CALA as the catalyst. The results indicated that the free CALA exhibited remarkable resistance to methanol and could be employed to produce biodiesel through a one-step methanol addition process. Furthermore, the free CALA demonstrated the capability to concurrently catalyse the transesterification of FPO (Frying Palm Oil) and the esterification of FFA to generate biodiesel even in the presence of excess water. Through response surface methodology (RSM) optimization, the following reaction conditions were identified as optimal: 16.6 wt. % water content and 5.5 wt. % lipase load, maintained at 30 °C for 22 hours. The impact of various reaction variables was observed to decrease in the sequence of water content > reaction time > lipase load. The calculated activation energy for biodiesel production stood at 32.96 kJ/mol, with kinetic parameters K'm and Vmax being 6.75 × 10−1 mol/L and 2.38 × 10−2 mol/(L·min), respectively. This research introduces an environmentally sound approach for manufacturing biodiesel using waste frying oil containing high levels of water and FFA as the source material, in conjunction with an economical free liquid lipase as the catalyst (17).

**11 Novel Catalyst Synthesised from Waste Glassware and Eggshells**

A distinctive methodology (19), was employed to successfully create a new catalyst. The catalyst precursor such as CaO-SiO2 was formed using discarded laboratory glass which possess SiO2, and lime (CaO) was obtained from discarded eggshells. This combination was further enhanced by incorporating cerium oxide to generate the innovative catalyst complex Ce-CaO-SiO2. Thorough characterization unveiled that the resulting catalyst possesses all the necessary attributes for effective biodiesel production. An extensive analysis of parameters was conducted, demonstrating the catalyst's efficacy. The optimal configuration of independent factors consisted of process temperature is about 70°C, duration of 100 minutes, methanol-to-oil molar ratio is 11, and amount of catalyst loading is about 3 wt.%. This configuration yielded a biodiesel output of 95.29 wt. %. Moreover, an examination of catalyst reusability indicated that it can be employed up to five times without experiencing notable activity reduction, affirming its viability for practical use. In conclusion, the synthesized catalyst exhibits remarkable efficiency and holds promise for biodiesel manufacturing.

**11.1 Bismuth Silicate-A Novel Catalyst for Biofuel Production:**

The study had involved in the novel application of Bismuth Silicate (such as Bi4Si3O12 and Bi2SiO5) based catalyst of three different forms, which are named to be 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 increase in the total acidity, surface area, band gap energies and volume of the pores was caused due to action of Ultrasound waves, which in turn reducing the time about 30min. 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 (20).

**11.2 Extraction Methodologies applied in Biofuel production:**

The extraction methods applied gets varied 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 from the different generation biomass are Conventional Solvent Extraction (CSE) for the first-generation feedstocks such as energy crops, Mechanical methods such as

expeller and oil press, CSE, Physical Support Solvent Extraction (PSSE), Supercritical Fluid Extraction (SFE) and other novel techniques can be applied for second generation feedstocks and the biofuels from third generation feedstocks can be extracted by applying the techniques such as CSE, PSSE, SFE and novel approaches. 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



**Fig 3: Production Process of Biofuels-Flow Diagram**

**11.3 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 brake specific energy consumption, analysis of heat flow patterns, friction power, emission levels of smoke are the parameters selected for their significance in fuel operation in diesel engines (21). These can be represented as in Fig 4.



**Fig 4: Evaluation Parameters for Biofuel Performances**

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

**12 Biofuel: Futuristic prospects:**

Small scale bio-refineries integrated along with the farms similar to the setup like 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 the conventional biofuels. Food wastes from the result of municipal wastes 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 to be applied in pilot and industrial levels of production. Enzyme immobilization using nanoparticles can contribute for higher conversion. Biofuels blended with conventional fuels can be encouraged. Then the efficiency of a biofuel is in need to be increased as well to encounter the daily needs of the people, which in turn to be used as fuel for routine by bypassing the use of fossil-based fuels. By the application of systems biology and computational biology, the microbial strains utilized for the biofuel production are improved by the strain improvement process which includes genome editing and engineering. 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.

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