

Biodiesel: Review on Production Techniques & Raw Material Process Economic Aspects

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Abstract:

Biodiesel is found to be one of the promising alternatives for conventional fuels since lot of researches and steps for practical implementation has been started by numerous countries to meet out the futuristic demands of switching towards new energy sources due to less toxicity and eco-friendly aspects. Diverse feedstock's are being used to produce by means of blending/direct use, micro-emulsion, thermal cracking/pyrolysis and transesterification. Parameters like type of alcohol, type of catalyst & its quantity, alcohol to oil ratio, stirring speed, temperature, pressure, time of reaction and type of source oil plays a major role in the contribution of yield, efficiency and cost. It is really important to study the process economics to understand the aspects in practical implementation. This study entirely deals with biodiesel production methods, parameters associated and process economics behind selection of raw materials.

Keywords: Biodiesel, Production, Process Economics, Raw materials, Feedstock

1. INTRODUCTION

Decrease in availability of mineral oils is becoming a biggest concern in terms of energy crisis. Mineral oil also leads a way for global warming, environmental degradation and pollution, green house effect etc.[1] Few statistics reveals that oil and gas will not be available for use after 63 years if it is used consistently in the same pace.[2] Thoughscientists are working hard in doing researches on the areas of wind, geothermal and solar technologies, there is a huge need of alternative renewable energy sources termed as bio fuelswhich is an emerging technique in the field of energy sector.

In recent trends, world is stepping forward for a renewable production source of alternative fuel for diesel which is beneficial to environment, non-toxic and bio-degradable.

In the vision of deficiency towards fossil fuels and a hike in demand of diesel for generation of power, agriculture and transportation [3] in very near future tends to identification and implementation of new alternative to avoid the crisis and an alternative is necessary and unavoidable in current scenario.

Biodiesel is produced from various biological resources which are renewable and non-toxic to environment such as fats and non-edible oils etc. which can be a best alternative for diesel. Biodiesel literally defined as a fuel with long chain fatty acids with mono-alkyl esters from oils and fats.[4] Numerous research studies prove that biodiesel can be a suitable alternative and substitute. Production techniques undergo speedy and comprehensive techno- revolution in academic and industries. Efficiency majorly deals with feedstock nature, catalyst, reaction time, temperature, alcohol type and economic aspects.[5]

In case of switching towards fuel of biodiesel, there records a neutral carbon since the quantity of emitted carbon will be same as adsorbed by plant/animal during its life time during combustion process makes a evidence of minimal emission during green combustion. In recent trends, domination of diesel may be high but for an alternative is truly need when we think in a futuristic approach and we can believe that biodiesel can be such a boon for the cause.

Key Characteristics of Pure Biodiesel

Certain key observation has to be done during the examination of pure biodiesel and the observations are being listed in the Table 1. [6]

S. No	Property	Observations
1	Anti-Foaming	Excellent
2	Cetane Number	45 & 70
3	Chemical Structure	Ester of fatty acids C ₂₂ , C ₁₆ , C ₁₂ , C ₁₄ &C ₁₈ .
4	Oxygen content	11%
5	Cold flow properties	Solidification become difficult to control and more rapid
6	Conductivity	500 pico S/m
7	Corrosion	Oxygen presence may contribute towards corrosion

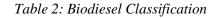
Table 1: Biodiesel Characteristics



Classification of Bio-fuel

Bio-fuels are broadly classified into three major categories based on their feedstock selection for production of bio-fuel named as first, second and third generation bio-fuels. The classification criteria and example of feed-stock is listed in Table 2. [7]

Generation	Definition	Feed-stock
First	Produced from food-crop or cultivated bio-energy	Direct usage of wheat,
	Crops	sorghum etc.
Second	Produced from Non-food feedstock such as agro	Residues from agro and
	and forestry stocks	food stock
Third	Produced from aquatic cultivated feedstock	Algae



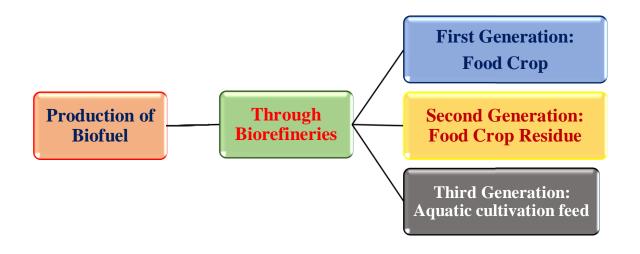


Figure 1: Classification of Biodiesel

2. Production of Biodiesel

The four main approaches for production of bio-diesel are [8]

- 1) Direct use and Blending
- 2) Transesterification Process
- 3) Thermal Cracking/Pyrolysis

4) Microemulsion

Direct use and Blending:

Usage of vegetable oils directly to engines as a fuel consists of numerous practical implementation issues with it. Considering those conditions, an alternative method of blending technique has been adopted and the method helps in obtaining the properties of a fuel to a considerable extent. This method helps us in overcoming the faced issues in practical approach. Blending help in improving quality and reducing consumption thereby play a promising role in approaching the alternatives.

S.NO	Biodiesel	Blender	Key Notes	References
1	E. sanguinea	Diesel	40% ES	[9]
2	Jatropha seeds	Diesel	20% JS	[10]
3	Rice bran	Ethanol	2.5 % E	[11]
4	Corn	Diesel	20% C	[12]
5	Soyabean	Diesel	20% S	[13]
6	Safflower oil	ULSD	50% B	[14]
7	Mahua fruit	Mineral diesel	30% MD	[15]

Successful ratio of 1:10 to 2:10 is preferred for running in a short period. Also there is a need of modifications in engine and customized running system for energy production since on usage without modifications lead to high risk and even danger of failure too.[16]

Transesterification Process

Glycerol and Biodiesel produced by combination of alcohol and triglycerides in vegetables leads to a reaction called as transesterification. The process takes place in the presence or absence of the catalyst which is determined by the quantity of feed stock free fatty acid which is directly related to important parameters like efficiency & production. It is a reversible process where reaction takes place usually under temperature/pressure. [17] The following equation depicts the simple transesterification reaction.

Triglyceride (C6H8O6) +CatalystAlcohol(ROH)Glycerol (C3H8O3) + Free fatty esters (C2H3O2R)



Generally transesterification takes place in different steps like acid, base, heterogeneous, lipase, supercritical, nano and ionic liquid catalysed process. [18] All the transesterification process looks similar but the change in catalyst plays a primary role in it.

Acid Catalysed

The reaction requires longer time and higher temperature. Sulphonic, hydrochloric and sulphuric acid are commonly used acid in the process.

Raw Material	Acid Used	Yield %	References
Refined soybean oil	Trifluoroacetic acid	98.4	[19]
Jatropha curcas oil	H ₂ SO ₄	95	[20]
Waste cooking oil	H ₂ SO ₄	89.6	[20]
Palm oil	CH ₃ OH-H ₂ SO ₄	83.72	[21]
Corn Oil	p-toluenesulfonic acid	100	[22]
Sunflower and Soyabean oil	H ₂ SO ₄	96.6	[23]

Table 4: Acid Catalysed Transesterification

Base Catalysed

The reaction is faster over here and corrosion is less but the process economics is higher due to catalyst consumption and issues in separation process. NaOH and KOH are commonly used catalyst in the process.

Table 5:	Base	Catalysed	Transesterification
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Raw material	Base used	Yield%	Reference
Jatropha Oil	NaOH	95.5	[24]
Soyabean Oil	NaOH	90	[25]
Cotton seed Oil	NaOH	98.5	[25]
Ceiba pentandra oil	КОН	96.2	[26]
Karanja oil	КОН	98	[27]
Sunflower cooking oil	КОН	99.5	[28]
Waste cooking oil	КОН	93.2	[29]



Heterogeneous catalysed

The reaction holds a great advantage of simpler separation and lower contamination enabling catalyst reusability. Potassium zirconias, Titanium and Amp. zirconia are few of theheterogeneous catalysts.

Raw material	Catalyst used	Yield%	Reference
Soyabean Oil	Titanium	95	[30]
Soyabean oil	Al doped Zirconias	95	[30]
Jatropha curcas oil	Solid Super Base CaO	93	[31]
Jojoba oil	CaO	96.3	[32]
Waste Cooking Oil	SO ₄ ²⁻ /TiO ₂ -ZrO ₂	96.7	[33]
PFAD	SO ₄ ²⁻ /TiO ₂ -ZrO ₂	98.9	[34]
Decanter Cake	SO ₄ ²⁻ /TiO ₂ -ZrO ₂	91	[35]

Table 6: Heterogeneous Catalysed Transesterification

Lipase catalysed

Though the cost and reaction time are quite more, utilizing enzymes become a recent trend as it help to produce a high purity product and supporting quite easier separation. Pseudomonas species, Rhizopus oryza, Novozym 435, Lipozyme TL are few enzymes utilized in the process.

Raw material	Catalyst used	Yield%	Reference
Jatropha oil	Pseudomonas fluorescens	72	[36]
Virgin Oil	Rhizopus oryzae	75	[37]
Waste vegetable oil	Rhizopus oryzae	80	[38]
Soyabean Oil	Rhizopus oryzae	92	[39]
Rapeseed Oil	Lipozyme TL	95	[40]
Jatropha Oil	Chromobacterium viscosum	71	[41]
Soyabean Oil	Candida antarctica	80	[42]

Table 7: Lipase Catalysed Transesterification



Supercritical Reaction

Considering immiscibility constraints, this type of reaction takes place under high temperature and pressure. It is non catalytic but takes very lesser time for reaction. Though methanol consumption and cost are higher, purity is good, separation is easier and it an eco friendly process.

Raw material	Optimum Conditions	Yield%	Reference
Rapeseed Oil	350°C & 14 MPa	95	[43]
Coconut Oil	350°C & 19 MPa	95	[44]
Palm Kernel Oil	350°C & 19 MPa	96	[44]
Sunflower seed oil	252°C & 24 MPa	95	[45]
Vegetable Oil	200°C & 20 MPa	80	[46]
RBD Palm oil	350°C & 40 MPa	95	[47]
Jatropha Oil	320°C & 8.4 MPa	100	[48]

Table 8: Supercritical Catalysed Transesterification

Nano Catalysed

This type of advanced catalyst enhances the catalytic activity due to its enormous advantages. It can be concluded as a promising one for effective production. Few of the nano catalysts are CaO/CaN, CaO/SS, CaO-Al2O3 etc.

Raw material	Catalyst used	Yield%	Reference
Palm Oil	SrO–CaO–Al ₂ O ₃	98.16	[49]
Soyabean Oil	CaO/CaN	93	[50]
Soyabean Oil	CaO/SS	96	[50]
Waste Cooking Oil	CaO	94.4	[51]
Waste Cooking Oil	CaO & MgO	98.95	[51]
Stillingia oil	KF/CaO–Fe ₃ O ₄	95	[52]
Chinese tallow seed oil	KF/CaO	96.8	[53]

Table 9: Nano Catalysed Transesterification



Ionic Liquid Catalysed

This type of catalyst helps us in formation of biphasic product at the end enabling quick separation. The process takes very less time compared to others and also helps us in reusability. 1-n-butyl-3methylimidazolium is one of the ionic liquid studied by many researchers.

Raw Material	Catalyst Used	Yield %	Reference
Rapeseed oil	1-butyl-3-methylimidazolium hydrogen sulfate	8.89	[54]
Soyabean Oil	Chloroaluminate	98.5	[55]
Cottonseed Oil	1-(4-Sulfonic acid) butylpyridinium hydrogen sulfate	92	[56]
Rapeseed oil	1-butylsulfonate-3-methyl imidazolium hydrogen sulfate	100	[54]
Soyabean Oil	Brønsted acidic ionic liquid	93.2	[57]
Waste Palm	butyl-methyl imidazolium hydrogensulfate	95.7	[58]
Cooking Oil			

Table 10: Ionic Catalysed Transesterification

Thermal Cracking/ Pyrolysis

Numerous small molecules formed due to breakage of bonds using heat between 400

– 600 °C with/without oxygen or with/without catalyst named as a chemical change called Pyrolysis. Among the different classes of production, fast pyrolysis is found to be best suited one for the production of biodiesel due to its simplicity and efficiency. The process should be made with at most care since small deviations may lead to different products and uncertainty in purity of the product. Also separation technique in post production is yet a challenging milestone in this type of process. Zeolites, Red-mud and Alumina are the commonly used catalyst in pyrolysis process.

Table 11: Thermal Cracking/Pyrolysis

Raw Material	Catalyst Used	Yield %	Reference
Waste olive oil	Dolomite	93	[59]
Rapeseed oil	ZSM-5	95	[60]

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Biomass tar	ZSM-5	75.56	[61]
Soybean oil	Bauxite	93	[62]
Vegetables oil	Sulfated zirconia	97.08	[63]
Sunflower oil	HZSM-5	83.13	[64]
Woody oil	Al ₂ O ₃ /MCM-41/CaO	90.1	[65]

Micro emulsions

Certain oil cannot be directly used as a fuel and viscosity might be one of the reasons for the particular cause. In this regard, micro-emulsions can be a best suitable one to overcome the cause. It really consists of oil, water and a surfactant which helps in incrementing the Cetane number and lowering the viscosity. This type of biodiesel cannot be used for a long time in a engine because it may cause damage to the engines. But literally thistype of fuel possesses best spray property when compared to others.

Table 12: Micro emulsions

S.No	Micro-emulsions	Reference
1	Ethanol – Vegetable Oil – Carboxylate	[66]
2	Ethanol – Palm Oil – Diesel	[67]
3	Ethanol – Jatropha Oil – Diesel	[68]
4	Ethanol – Jatropha Oil – Sorbitane Fatty esters	[69]
5	Rhamnolipid – Crude Glycerine – Diesel	[70]

3. Discussion of Key Variables involved in Biodiesel Characteristics

Key variables associate with Biodiesel production are selection of type of alcohol needed, Alcohol to Oil Ratio, Time of the reaction, Temperature needed, Necessity of mixing, type of catalyst and its quantity, pressure etc. Each variable has its own characteristic contribution towards the economical, simple and quicker process for biodiesel production.

Selection of Oil

The most important entity required for the biodiesel production is Oil source. Selection of oil is done based on analyzing its physicochemical characteristics like viscosity,

calorific value etc. which help us to identify the suitable oil which as a primary base raw material for biodiesel production. Also few parameters like iodine index, acidity, phosphorous index and oxidation stability are quality based parameters studied before selection of oil source. Also fatty acid content deals with the production process in a major extent since catalyst selection greatly deals with it. [71] Jatropha, rapeseed, sunflower, palm, soybean, cotton etc. are the most commonly used raw material for producing oil.

Type of Alcohol

As we are aware that alcohol reacts with triglycerides to form free fatty acids. Thus alcohol is a major raw material required for the process to complete the reaction.[72] Ethanoland Methanol are most commonly used alcohols in the production process due to its availability physical & chemical advantages and low cost. There are other few alcohols used in process like butanol, octanol, branched alcohols etc. but they are costly. Also few co- solvent with alcohol for better yield purpose has been reported in few researches but majorly Methanol is using by extensive researchers in their research.

Alcohol to Oil Ratio:

An important parameter associated with yield, cost and conversion is alcohol to oil ratio. Literally when conversion needs to occur in a shorter time, alcohol to oil ratio should be higher and it may be lead to higher to purity of biodiesel.[73] The alcohol to oil ratio reported in various literatures vary from 1:1 to 45:1 in different methods of production of biodiesel. This ratio selection makes a huge impact until the biodiesel refining process.

Time of reaction, Stirring speed, Temperature and Pressure

All the parameters are interlinked with each other and we can infer that the above parameters deal with overall production time, quantity and cost. Reaction time is one which deals with quantity of production and cost of production. Only few process required stirring when viscosity variance occurs during the reaction. Temperature and Pressure is varied only when the reaction is too low and this type of reaction occurs under special category only. Also all these parameters deal with yield, conversion efficiency & purity of production.[74]

Type of Catalyst and Quantity

Quantity of catalyst and the type of the catalyst used for the reaction is directly proportional to biodiesel yield and conversion efficiency since the catalyst increase the speed

of the reaction thereby enabling increase in yield. There are several type of catalyst available like acid, basic, ionic, nano etc. and the catalyst is selected for the reaction on the basis of oil source characteristics.[75]

Other parameters

Selection of appropriate blend quantity and the selection of required quantity of emulsions for the preparation of biodiesel play a major role in blending and micro-emulsions techniques respectively in which those parameters meant to deal with yield and efficiency aspects.

4. Process Economics dealing with Raw Material

Process Economics is one of the important aspects to be studied in all the areas of engineering, science and technology as it paves a successful way for the practical implementation of the idea or research aspects. [76] World due to its adverse effects facing in the areas of environment protection and its related health hazards taking a joint initiative to save the earth. Also Government has started using blending technique as a miniature alternative for this futuristic idea. But a prominent alternative really needed and Biodiesel found to be a boon for the conventional fossil fuels. In this regard, it should be economical tobring out for human consumption in daily needs.

Oil, Alcohol and Catalyst are the primary raw materials involved in this process. As discussed earlier in this study, Methanol is commonly used as an alcohol due to its availability and low cost in several processes.[72] Though co-solvents used in few studies, it is added in a very minimal amount and it does not make a much variation. Catalyst is another challenge but numerous studies worked up in biodiesel production consumes very less amount of catalyst and also the most of the catalyst used as easily available and of considerable cost.[75]

The only thing we need to study is the oil source and its availability for its implementation in practical applications. Jatropha, rapeseed, cottonseed, palm, vegetable, sunflower, soybean and waste cooking oil are commonly used source for oil.[77] In this area, cottonseed, palm, sunflower, vegetable, rapeseed and soybean oil are being used in the areas of cooking and wide extensive use of those oils in production of biodiesel may make a huge impact on the food market chain and oil price may reach a hike. Also collection of waste cooking oil is really a challenging task in preparing biodiesel. Thus we can infer that

Jatropha oil, non edible oil found to be a boon for the biodiesel production industry. Also statistics says that Jatropha cultivation has been increased gradually to a great extent in past 10 years giving a hope towards switching an alternative fuel for usage.

Jatropha oil cost around Rs. 8-10 per litre and NaOH can be used a catalyst since the research stated the highest yield using the same in adding methanol in the ratio of 5:1. We can conclude in the aspects of raw material process economics that Jatropha Oil found to be aboon to biodiesel production.

5. Conclusion

The following points were inferred during this study in the process economic aspects of biodiesel production:

- 1) As we are aware, Methanol can be used a alcohol in the process considering availability and low cost
- 2) Base Catalyst is preferred due to its low cost and availability
- 3) Jatropha Oil is economical for this process and can be used in biodiesel production to meet out the problems which we are going to face in our future.
- 4) Since methanol to oil ratio is low while using base catalysts, overall process cost is also low enabling the public to change their mind towards quick shift for the biodiesel usage as an alternative fuel.
- 5) Also there is no need of making quite huge modifications in engine system while implementation for practical use.
- 6) Production process in simpler proving high purity and easier separation of the components.

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