Technologies for Biodiesel Production from Non-edible Oils: A Review

V. R. Kattimani^{1*} and B. M. Venkatesha²

¹Department of Chemistry, Yuvaraja's College, University of Mysore-570005, Karnataka, India; veeranna_rk@yahoo.co.in ²Department of Chemistry, Yuvaraja's College, University of Mysore-570005, Karnataka, India; venkichem123@yahoo.in

Abstract

Biodiesel is an alternative eco-friendly diesel fuel. Currently, the cost of biodiesel is higher than the conventional diesel oil due to the usage of expensive edible oil. Hence, in this paper we reviewed the research work that has been done in the area of non-edible oil to produce cost effective biodiesel. Biodiesel can be made economically viable if non-edible oil of sources that are available locally is considered.

Keywords: Biodiesel, Non-edible Oil, Energy Source.

1. Introduction

Limited conventional energy resources and increasing stringent environmental regulations have motivated an intense search for an alternative to diesel oil. In addition, the highly fluctuating global crude oil prices have negative impact on the economy of many countries especially oil importing countries like India [1]. Apparently, biodiesel is gaining worldwide attention as an alternative to diesel oil because of its renewability, eco friendly nature. Chemically, biodiesel is defined as the alkyl monoesters of fatty acids obtained from sources such as vegetable oil, animal fat, frying oil, and restaurant waste oil [2]. One of the main characteristics of biodiesel is that its use does not require any major modifications in the existing diesel engine [3]. However, the feedstock and production cost of biodiesel are the main hurdle for the wide spread commercial use of biodiesel. Biodiesel price can be reduced by using high free fatty acid feedstock like non edible oils because most of them are available at nominal price. It includes jatropha, karanja, mahua, linseed, rubber seed, neem, cotton seed, soapnut oil etc.

The biodiesel cost is approximately 1.5 to 2% higher than conventional diesel oil and is due to the use of food grade edible oil [4]. Table 1 show the distribution of the biodiesel production cost in general and indicates that cost of feedstock is the major contributor (70.60%) in the biodiesel production cost.

2. Biodiesel Production Methods

2.1 Transesterification Process

It is the most commonly used method for the production of biodiesel [5]. The process of separating fatty acids from glycerol backbone to produce fatty acid esters (FAE) is commonly known as biodiesel [6]. This process occurs stepwise with monoglycerides and diglycerides as intermediate products. Figure 1 shows a simple molecular representation of the transesterification process [7].

Transesterification process is classified as alkaline catalyzed, acid catalyzed esterification, acid- alkaline catalyzed (Two stage) and non catalyzed supercritical (SAKA process), enzyme catalyzed and heterogeneous catalyzed

^{*}Corresponding author:

process. This can also be carried out via radio frequency microwaves.

2.1.1 Alkaline Catalyzed Transesterification **Process**

This process is most effective for feedstock with FFA level below 2% as it is reported to proceed about 4000 times faster than acid catalyzed esterification process [8]. In this process homogeneous base catalysts such as sodium methoxide, sodium hydroxide, and potassium methoxide potassium hydroxides have been successes fully used at industrial level for the production of bio diesel. It becomes ineffective when free fatty acid level exceeds 2% because FFA reacts with the most common alkaline catalyst and forms soap which inhibits the separation of ester from glycerin. It reduces the conversion rate. The acid values of most of the inedible oils are higher than the performance range of base catalyst. The inedible oils such as rubber oil, tobacco oil, mahua oil and soapnut oil contain 17%, 35%, 19%, 9.1% FFA respectively [9, 10]. FFA level of more than 2% alkaline catalyzed transesterification process becomes ineffective in converting the above oil into biodiesel. Figure 2 shows the process diagram for alkaline catalyzed

Table 1. Distribution of biodiesel production cost

•	
Materials	Cost %
Feedstock	70.60
Maintenance	4.00
Chemicals	12.60
Energy	2.70
Labor	2.50
Depreciation	7.60

Source: Arjun et al. [4].

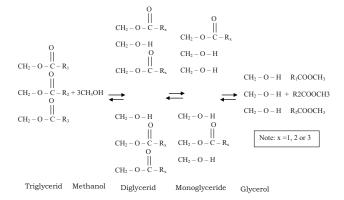


Figure 1. Molecular representation of transesterification process.

transesterification process [11]. The Table 2 represent the summary of research work that has been done by many researcher in the area of biodiesel from non edible oil using alkaline catalysed trans-esterification process.

2.1.2 Acid Catalyzed Transesterification Process

In these process catalysts like sulphuric acid, organic sulponic acids, phosphoric acid and hydrochloric acids are used as acid catalyst. Considerable research work [14, 15] has been done to use acid catalysts for the transesterification of inedible oil. Table 3 shows the summery of research work that has been done by many researchers in the area of biodiesel production from inedible oil by using acid catalyzed transesterification process. FFA level of most of the inedible oils are higher than 2% so in these cases acid catalysts are used. However, it requires higher amount of alcohol, higher reaction temperature and pressure, and lower reaction rate [16]. Figure 3 shows the process diagram for acid catalyzed transesterification process.

2.1.3 Acid-alkaline Catalyzed (Two Stages)

Generally, this process is recommended for the feedstock that has higher FFA level (>2%). In this process, both acid and alkaline catalysts are used. In the first stage, oils are reacted with alcohol in presence of acid catalyst. The acid value of the product is reduced to alkaline transesterification range (i.e. < 2%) and in the second stage; the oil is retreated with alcohol in the presence of alkaline catalyst [18]. Figure 4 shows the acid alkaline catalyzed transesterification process. Table 4 shows the summary of research work that has been done by many researchers in the area of biodiesel production from inedible oil by using acid- alkaline catalyzed transesterification process.

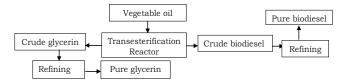


Figure 2. Process diagram for alkaline catalyzed transesterification process.

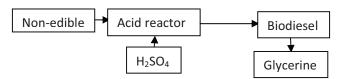


Figure 3. Process diagram for acid catalyzed transesterification process.

Table 2. Reaction conditions for alkaline catalyzed transesterification process for inedible oil

Type of feedstock	Molar ratio(alcohol to oil)	Type and amount of catalyst (%)	Reaction time in minutes	Reaction Temperature in K	Reference
Tobacco oil	18:1	KOH, 1%	25	333	[12]
Cotton seed oil	135:1	NaOH, 0.1mol/L in methanol	180	313	[13]

Table 3. Reaction conditions for acid catalyzed transesterification process for inedible oil

Type of	Molar ratio	Type and amount of	Reaction time	Reaction	Reference
feedstock	(alcohol to oil)	catalyst (%)	in min	Temperature in K	
Tobacco oil	7:1	H ₂ SO ₄ , 1% with lower molar ratio and 2% with higher molar ratio	20	333	[12]
Mahua oil	10:1	H ₂ SO ₄ , 0.3% to 0.35% v/v	60	333	[17]

Table 4. Reaction conditions for acid -alkaline catalyzed transesterification process for inedible oil

Type of feedstock	Molar ratio(alcohol	Type and amount	Reaction time in	Reaction Temperature
	to oil)	of catalyst	min	in K
		(%)		
	18:1	H ₂ SO ₄ , 1%		
Tobacco		to 2 % v/v	60	333
oil	6:1	KOH, 1%		
		w/v		
	0.30 to	H ₂ SO ₄ , 1%		
Mahua oil	0.35% v/v	v/v	60	333
	0.25% v/v	KOH, 0.7%	00	
		w/v		
	6:1	H ₂ SO ₄ , 0.5%	30	
Rubber		v/v	30	318
seed oil	9:1	NaOH,	30	310
		0.5% w/v	30	

Source: Sharma et al. [9]

2.1.4 Non Catalyzed Supercritical (SAKA Process)

The use of an acid or alkaline catalyst results in more complex process. To overcome the limitations of acid and base catalyzed transesterification process, a new technology called non catalyzed super critical methanol transesterification has been developed [19, 20]. Supercritical fluids have diffusivities like gas and viscosity like liquid.

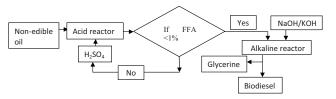


Figure 4. Process diagram for acid- alkaline catalyzed transesterification process.

This process requires very short time (only 4 minutes) for the completion of the process under super critical conditions (temperature 350°C to 400°C and pressure more than 80 bar). This process requires no catalyst and is not affected by the presence of water and FFA [19]. However, it requires high alcohol to oil (42: 1) molar ratio and higher capital and operating cost. It also consumes more electric power. Figure 5 shows the process diagram for non-catalyzed supercritical methanol method. Table 5 summarizes the work that has been done in the area of biodiesel production from inedible oils by using non-catalyzed supercritical methanol method.

2.1.5 Enzyme Catalyzed Transesterification **Process**

Bio catalytic transesterification process can be used for the biodiesel production. This process can be carried out

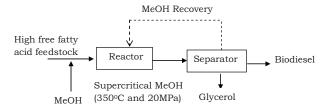


Figure 5. Process diagram for Supercritical methanol non-catalyzed transesterification process.

in the presence of enzyme such as lipase. This process has many advantages over conventional transesterification process like generation of zero by byproducts, no difficulty in product separation. It requires moderate process conditions (temperature 35°C to 45°C) [21]. In this process catalysts can be recycled easily. This process can successfully be used for the transesterification of inedible oil because enzymatic reactions are insensitive to FFA level and water contain of the oil [22].

2.1.6 Heterogeneous Catalyzed Process

In this process, both acid and base solid catalysts are used. Acid heterogeneous catalysts such as sulfated metal oxides, heteropolyacids, sulphonated amorphous carbon and acid ion exchange resin [23, 24] are extensively used for the production of biodiesel from inedible oil. Base heterogeneous catalyst such as metal oxides, zeolites, hydrotalcites and anion exchange resins are used in biodiesel productions [25]. The use of heterogeneous catalyst does not yield soap. However, some solid metal oxides like tin, magnesium, zinc results in metal soap or metal glycerates this problem can be eliminated by using a complete heterogeneous catalyst. Solid base catalysts are more active than solid acid catalyst. Cao is most extensively used as a solid base catalyst as it poses many advantages such as longer catalyst life, higher activity and requires moderate reaction condition.

Heterogeneous catalyzed transesterification process can tolerate extreme reaction conditions than homogeneous catalyzed transesterification process.

2.1.7 Microwaves Assisted Synthesis Process

Pharmaceutical industries are using microwave assisted synthesis process extensively [26]. Few studies [27] have conducted to use microwave assisted transesterification process. This process is similar to conventional transesterification wherein conventional heating is replaced

Supercritical methanol non-catalyzed transesterification process for inedible oil

Variables	Supercritical methanol method
Type of alcohol	Methanol
Reaction time (min)	7–15
Reaction temperature (°C)	340-385
Reaction pressure (MPa)	10-25
Type of catalyst	None
Methyl ester yield	98
Removal for purification	Methanol
Free fatty acids	Methyl esters, water
Smelling from exhaust	Sweet smell

with microwave to facilitate the reaction. The yield is also seems to be better while minimizing the processing time. Experiments have conducted at various power inputs ranging from 160W to 800W at particular temperature. Maximum yield 93.8% was reported at 160W for rice bran oil [27].

2.2 Availability of Edible and Non-edible Oil in India

India is the world's largest importer edible oil followed by European Union and China. India is the world's thirdlargest consumer after China and the EU. A growing population, increasing rate of consumption and increasing per capita income are accelerating the demand for edible oil in India.

Solvent Extractors Association data indicates that India's edible oil imports has increased to 6.12 lakh tonnes in the fiscal ended March 2010 while the non-edible oil imports has fallen to 20,575 tonnes.

The country had imported 6.41 lakh tonnes of vegetable oils comprising edible and non-edible oil in March 2009. However, the overall import of vegetable oils rose 4.3% to 37.47 lakh tonnes during November 2009 to March 2010 compared with 35.92 lakh tonnes in the corresponding period of the previous year. Non-edible oil imports rose by 2.5% to 1.62 lakh tonnes during November 2009 to March 2010 compared with 1.58 lakh tonnes in the year-ago period, while edible oils imports increased to 35.85 lakh tonnes from 34.34 lakh tonnes. A large gap is there between the demand and supply. India is importing larger quantity of edible oil. Hence, it is economically viable to produce biodiesel from non-edible oil because most of these are available locally. Most of the non edible oils sources can be grown on waste land.

3. References

- 1. Van Gerpen J (2005). Biodiesel processing and production, Fuel Processing Technology, vol 86(10), 1097-1107.
- 2. Canakci M (2007). The potential of restaurant waste lipids as biodiesel sources, Bioresource Technology, vol 98(1), 183-190.
- 3. Enweremadu C C, Mbarawa M M (2009). Technical aspects of production and analysis of biodiesel from used cooking oil-a review, Renewable and Sustainable Energy Reviews, vol 13(9), 2205-2224.
- 4. Arjun B, Chhetri K et al. (2008). Waste cooking oil as an alternative feedstock for biodiesel production, Energies, vol 1, 3-18.
- 5. Demirbas A (2009). Progress and recent trends in biodiesel fuels, Energy Conversion and Management, vol 50(1), 14 - 34.
- 6. Ma F R, and Hanna M A (1999). Biodiesel production: a review, Bioresource Technology, vol 70(1), 1-15.
- 7. Felizardo P, Correis M J N et al. (2006). Production of biodiesel from waste frying oils, Waste Management, vol 26(5), 487-494.
- 8. Helwani Z, Othman M R et al. (2009). Technologies for production of biodiesel focusing on green catalytic techniques: a review, Fuel Processing Technology, vol 90(12), 502-1514.
- 9. Sharma Y C, Singh B et al. (2008). Advancement in development and characterization of biodiesel: a review, Fuel, vol 87(12), 2355–2373.
- 10. Chhetri A B, Tango M S et al. (2008). Non-edible plant oils as new sources for biodiesel production, Journal of Molecular Sciences, vol 9(2), 169-180.
- 11. Math M C, Kumar S P et al. (2010). Technologies for biodiesel production from used cooking oil: a review, Energy for Sustainable Development, vol 14(4), 339-345.
- 12. Veljkovic V B, Lakicevic S H et al. (2006). Biodiesel production from tobacco (Nicotiana tobacum) seed oil with high content of free fatty acids, Fuel, vol 85(17-18), 2671-2675.
- 13. Qian J, Wang F et al. (2008). In situ alkaline transesterification of cotton seed oil for production of biodiesel and non-toxic cotton seed meal, Bioresource Technology, vol 99(18), 9009-9012.
- 14. Marchetti J M, Miguel V U et al. (2007). Possible methods for biodiesel production, Renewable and Sustainable Energy Reviews, vol 11(6), 1300-1311.

- 15. Noureddini H, and Zhu D (1997). Kinetics of transesterification of soybean oil, Journal of American Oil Chemists' Society, vol 74(11), 1457-1463.
- 16. Stamenkovic O S, Lazic M L et al. (2007). The effect of agitation intensity on alkali-catalyzed methanolysis of sunflower oil, Bioresource Technology, vol 98(14), 2688-2699.
- 17. Ghadge S V, and Raheman H (2005). Biodiesel production from Mahua (Madhuca Indica) oil having high free fatty acids, Biomass and Bioenergy, vol 28(6), 601-605.
- 18. Math M C, and Irfan G (2007). Optimization of restaurant waste oil methyl ester yield, Journal of Scientific and Industrial Research, vol 66, 772-776.
- 19. Kusdiana D, and Saka S (2002). Kinetics of transesterification in rapeseed oil to biodiesel fuels as treated in supercritical methanol, Fuel, vol 80(5), 693-698.
- 20. Demirbas A (2003). Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterification and other methods: a survey, Energy Conversion and Management, vol 44(13), 2093-2109.
- 21. Hama S, Yamaji H et al. (2004). Effect of fatty acid membrane composition on whole-cell biocatalysts for biodiesel-fuel production, Biochemical Engineering Journal, vol 21(2), 155-160.
- 22. Du W, Xu Y et al. (2004). Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors, Journal of Molecular Catalysis B Enzymatic, vol 30(3-4), 125-129.
- 23. Arzamendi G, Campoa l et al. (2007). Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts; comparison with homogeneous NaOH, Chemical Engineering Journal, vol 134(1-3), 123-130.
- 24. Antunes W M, Veloso C O et al. (2008). Transesterification of soybean oil with methanol catalyzed by basic solids, Catalysis Today, vol 133-135, 548-554.
- 25. Singh A K, and Fernando S D (2007). Reaction kinetics of soybean oil transesterification using heterogeneous metal oxide catalysts, Chemical Engineering Technology, vol 30(12), 1716-1720.
- 26. Alcar J, Diels G et al. (2007). Microwave assisted medicinal chemistry-mini review, Medicinal Chemistry, vol 7(4), 345-369.
- 27. Ramakrishnan K, Kudchadker A P et al. (2010). Microwave assisted transesterification of rice bran oil, Journal of Engineering Research and studies, vol 1(1), 165–170.