BIODIESEL PRODUCTION USING CONTINUOUS ULTRASONICATION OF NON-EDIBLE OILS

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
Of
INTEGRATED DUAL DEGREE
(Bachelor of Technology and Master of Technology)
In
CHEMICAL ENGINEERING
(With specialization in Hydrocarbon Engineering)

By

POKALA CHAKRADHAR

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE-247667 (INDIA)
MAY, 2016

DECLARATION

I hereby assure that the work presented in this project report entitled **“Biodiesel Production using Continuous Ultrasonication of Non-edible oils”** is submitted in partial fulfilment of the requirement for the award of the degree of, **“Integrated Dual Degree (Bachelor of Technology and Master of Technology) in Chemical Engineering”** with specialization in **“Hydrocarbon Engineering”** is an authentic record of my work carried out under the supervision of **Dr. Vimal Kumar**, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this report has not been submitted by me for the award of any other degree of this institution or any other institution.

Place: Roorkee **Pokala Chakradhar**

Date:

CERTIFICATE

This is to certify that Mr. Pokala Chakradhar has completed the research project report entitled **“Biodiesel production using continuous ultrasonication of non-edible oils”** under my supervision. This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Dr. Vimal Kumar
Associate Professor
Department of Chemical Engineering
Indian Institute of Technology Roorkee, Roorkee

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Pokala Chakradhar

ABSTRACT

The present work focuses on biodiesel production from non-edible oils using continuous ultrasonication. The use of non-edible oils as a feedstock improves the economy of biodiesel production. Further, the process intensification techniques, such as ultrasonic irradiation enhances the mass transfer rate between the reactants which are immiscible and thereby reduces the reaction time and improves production yield. When compared to batch process, using continuous ultrasonication assisted transesterification process improves the overall economic effect, providing a lower production cost, uniform product quality and easier control of the process and decreases the reactor volume by reducing retention time required to achieve the desired degree of triglycerides conversion.

In the present work, jatropha curcas oil was converted to biodiesel in a two-step process. In the first step, esterification of jatropha curcas oil was carried out with methanol in the presence of sulphuric acid catalyst in batch process. Second step involves transesterification of esterified jatropha curcas oil with methanol in continuous process using ultrasonication at a temperature of 35- 40 ^{0}C. Sodium methoxide with 1 wt. % of oil was used as base catalyst and 6:1 methanol to oil molar ratio was taken. Experiments were designed using Central Composite Design (CCD) in Response Surface Methodology (RSM) in Design Expert software to determine the optimized process parameters. Amplitude, pulse ratio and flowrate are taken as process variables. Maximum FAME conversion was determined to be 77.21 % and was obtained at 80 % amplitude, 80 % pulse ratio and 4 mL/min total flowrate. Highest biodiesel yield obtained was 70.82 % at same operating conditions. Parameter optimization is done and optimized conditions were determined to be 64 % amplitude, 80 % pulse ratio and 3.5 mL/min total flowrate where FAME conversion and biodiesel yield were found to be 76.84 % and 70.25 % respectively and were in good agreement with the predicted values. Properties of produced biodiesel such as specific gravity, flash point and fire point, cloud point and pour point at these conditions were matching with the EN 14214 specifications for standard biodiesel. Energy consumed per gram of biodiesel produced is less using ultrasonication process which makes the process energy efficient.

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CHAPTER 1

INTRODUCTION

1.1 General

Energy is one of the backbone for the economic growth of any country. In case of the developing countries like India, the energy sector assumes a critical importance in view of the ever increasing energy needs requiring massive investments to match them. India stands fourth in energy consumption in the world after USA, Republic of China and Russia. Currently, India's energy consumption has been increasing at a reasonably fast rate due to population growth and economic development. With rapid urbanization and improving standards of living of millions of Indian households, the demand is likely to grow significantly. To meet this energy demand, India imports about 72% of its crude oil.

The major sources for commercial energy in India are coal and crude oil, which are non-renewable in nature. While coal is abundant, it is regionally concentrated and is of low calorific value and high ash content, though it has the advantage of low sulphur content. Coal is the most important fossil fuel and accounts for 55% of the country energy needs. India was the fourth largest consumer of crude oil in the world and most of it is imported from Middle East countries. For the security of energy supply, it is necessary to insure about large pool of energy resource to enhance our economic growth. Energy conservation and increased use of renewable energy sources are the two paths, which can meet the supply demand imbalance of energy.

1.2 Renewable Energy

Energy can be categorized as renewable and non-renewable energy. Renewable energy is the energy which is obtained from sources that replete with time, such as solar power, wind power, tidal energy, geothermal power, hydroelectric power and biomass energy. The most salient feature of renewable energy is that it can be trapped without the liberation of detrimental pollutants. Non-renewable energy includes conventional fossil fuels such as coal, petroleum and natural gas, which are likely to deplete with time.

The substantial drivers for renewable energy are:

- Large gap in energy demand and supply, especially due to increase in population

- Limited reserves of non-renewable energy sources
- Lot of untapped potential
- Environmental concern
- Need for strengthening of India’s energy security
- Need for reduction of high emissions from industries
- A feasible solution for rural electrification

India has an estimate renewable potential of 249,188 MW out of which only 13.56% was installed at 33,791.8 MW as on 31st December 2014. The estimated potential and cumulative installed capacity of renewable energy sources are given in Table 1.1.

Table 1.1 Renewable energy in India (Source: www.mnre.gov.in, accessed on 2nd March 2016)

Sector	**Potential (MW)**	**Installed Capacity (MW)**	**% Achieved**
Wind Energy	102772	22465	21.86
Solar Energy	100000	3062.7	3.06
Small Hydro Power	20000	3990.9	19.96
Biomass	17536	1365.2	7.79
Bagasse Cogeneration	5000	2800.4	56.01
Waste to Energy	3880	107.6	2.77
Total	249188	33791.8	13.56

The installed capacity of different renewable energy sources is shown in Figure 1.1. Wind energy contributes more than 65% of the total installed capacity followed by hydro power and solar energy. In the case of biomass energy, only 7.79 % of estimated potential has been installed.

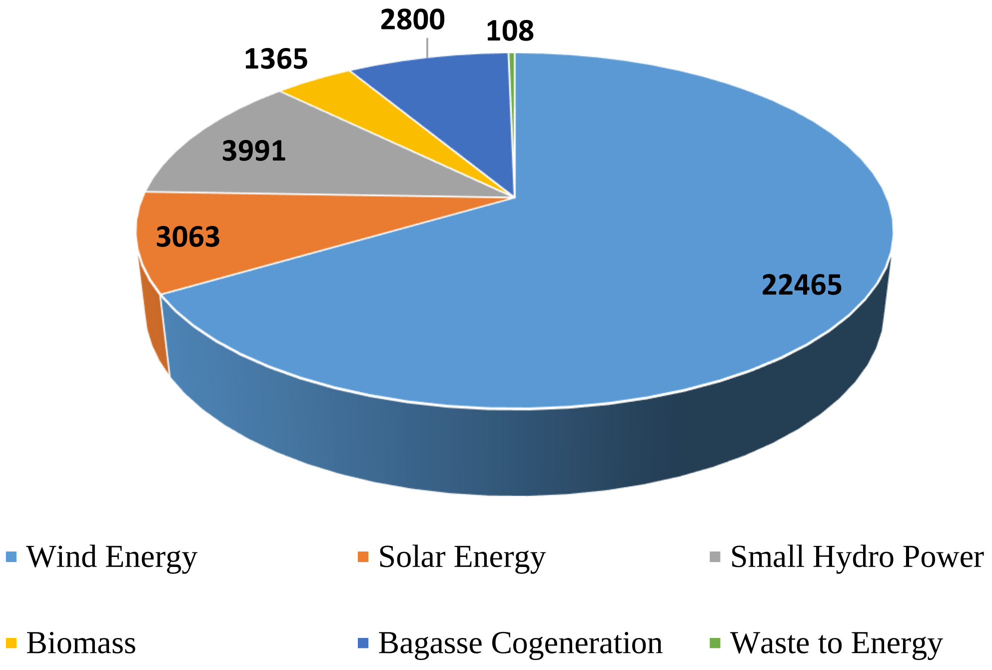


Figure 1.1 Installed capacity (MW) of different renewable energy sources in India

(Source: www.mnre.gov.in, accessed on 2nd March 2016)

1.3 Transportation Sector

Transportation sector consume largest portion of total power resources in the world. Major portion of crude oil consumption is used for the production of petrol, diesel and aviation fuel which are mainly used in transportation sector. According to the statistics published by International Energy Agency (IEA) on share of oil consumption in different sectors between 1973 and 2012, the transportation sector consumes maximum oil.

Amount of oil consumption has increased tremendously in the last four decades. Total oil consumption from 1971 to 2012 is shown in Figure 1.2. Worldwide oil consumption in 1973 and 2012 is estimated to be 2251 Mtoe and 3256 Mtoe respectively. Share of oil consumption in various sectors is shown in Figure 1.3. In 1973, the share of transportation sector was 45.4% which was increased to 63.7% in 2012. This increase of share in transport sector is due to increasing population, urbanization, increasing demand for auto motives, increased frequency of mobilization and obsoletion of animal power in transport sector. The decrease in oil consumption in industry sector may be due to the generation of electricity by steam.

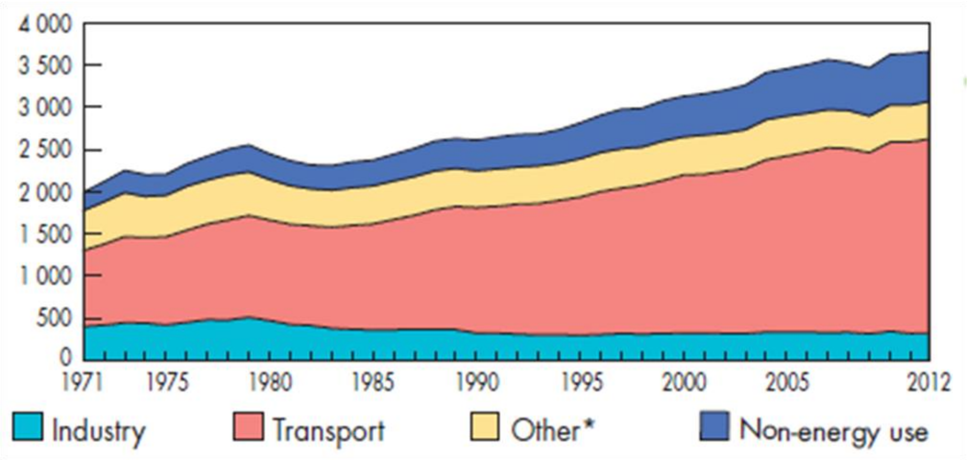


Figure 1.2 Total Oil Consumption (Mtoe) from 1971 to 2012 by sector (Source: www.iea.org, accessed on 29th April 2016)

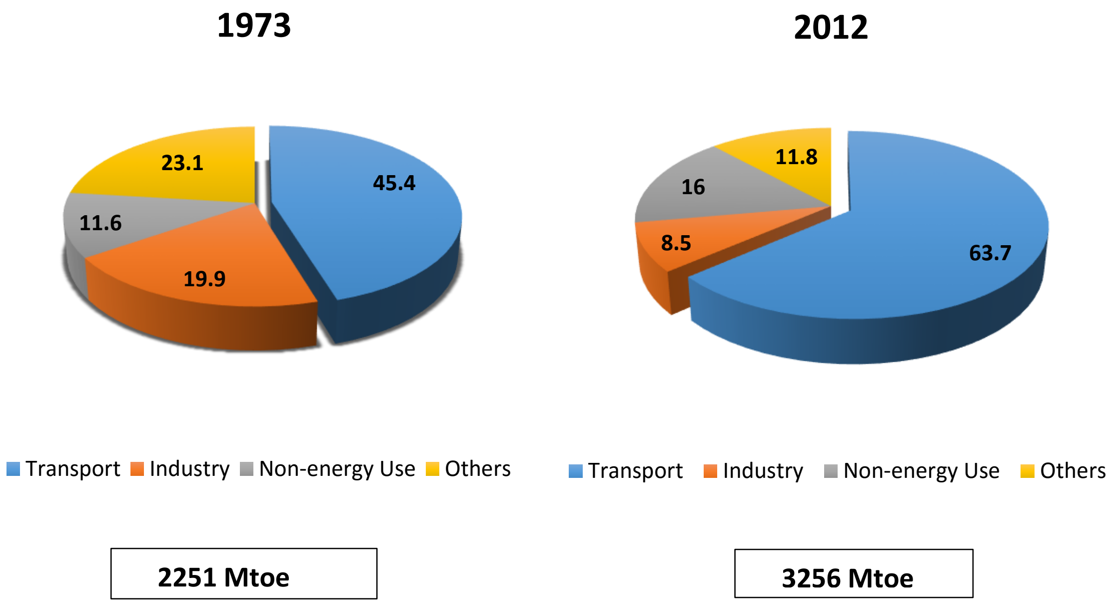


Figure 1.3 Shares of oil consumption by sector in 1973 and 2012 (Source: www.iea.org)

(Note: Others includes agriculture, commercial and public services, residential and non-specified other.)

1.4. Diesel Fuel

Diesel technology is playing a key role in all sectors of Indian economy due to its unique advantages which include high energy efficiency, power delivered, durability and reliability. Diesel is mainly used in the road transport, agriculture, industry and power generation sectors. Figure 1.4 shows all India end-user share in retail in 2012-13.

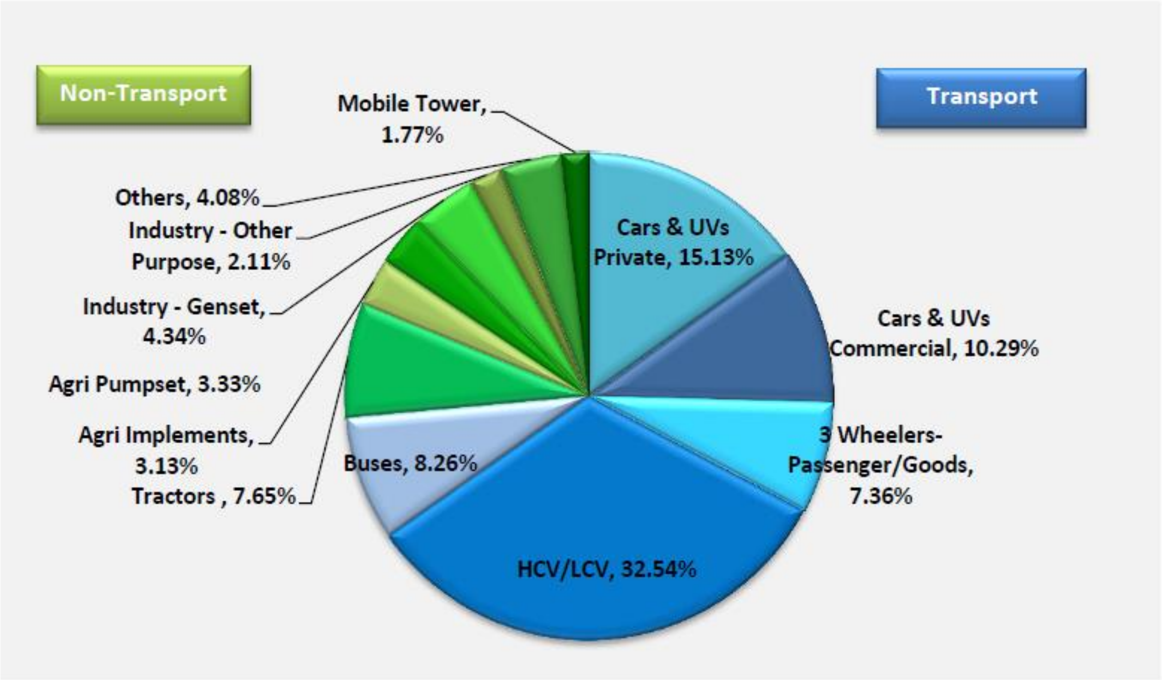


Figure 1.4 All India end user share (%) of Diesel in retail in 2012-13 (Source: http://ppac.org.in/, accessed on 1st November 2015) (HCV- Heavy Commercial Vehicles, LCV- Light Commercial Vehicles, UV- Utility Vehicles).

At all India level, diesel consumption is maximum in HCV/ LCV followed by private cars and UVs. In the non-transport sector, maximum consumption is in agriculture (tractors). This is because tractors are not necessarily used only for agricultural purposes. Today, they are also used for commercial purposes, such as for transporting construction material like bricks, stones, mined sand as well as other goods. The cost involved remains low for using tractors for the transportation of these materials not only due to lesser fuel consumption, but also because these vehicle enjoy various exemptions like not having to pay toll on highways.

Figure 1.5 shows the trend in consumption of diesel in India over a period of 32 years. The consumption of diesel increased from 3.84 Million Tonnes in 1975-76 to 69.08 Million tonnes in 2012-13. Although, diesel power, like other fossil fuel-based technologies, contributes to greenhouse gas emissions, its 20-40 percent greater efficiency also offers a feasible and readily available strategy to help reduce these same emissions and the amount of fossil fuels used in the transportation sector. Clean and green diesel is one of many technologies which includes the use of bioethanol, biodiesel and hybrid electric power that have potential for reducing energy consumption and greenhouse gas emissions.

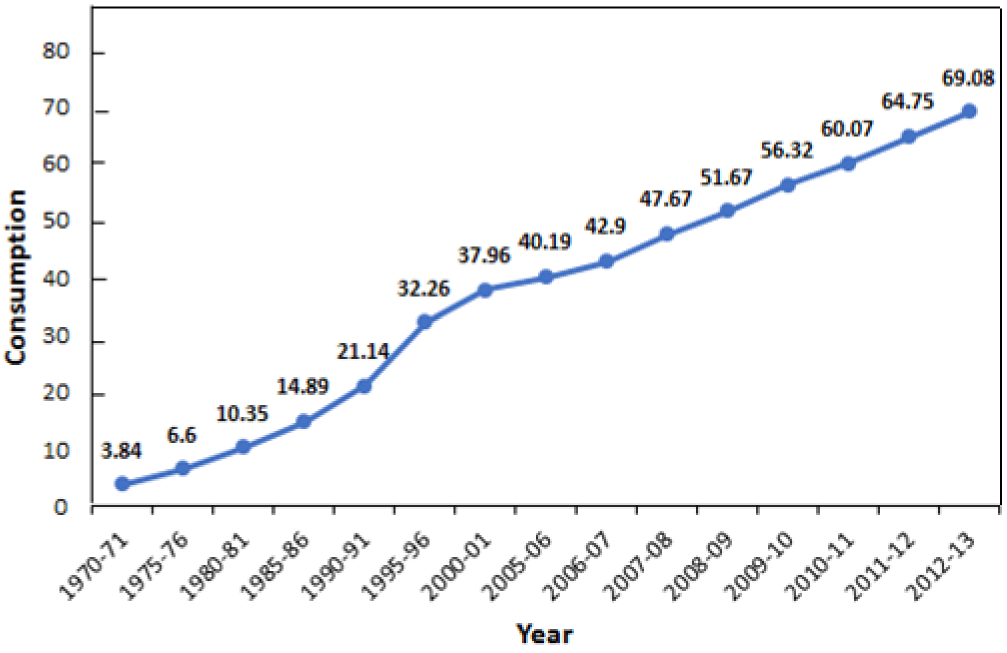


Figure 1.5 Trends in consumption of Diesel in India (Million Tonnes)

(Source: http://ppac.org.in/, accessed on 1st November 2015)

1.5. Biodiesel

Biodiesel is technically defined as the fatty acid alkyl esters derived from vegetable oils or animal fats that meet certain specifications of petroleum diesel. Biodiesel is a renewable fuel and is made from triglycerides that are present in vegetable oils or animal fats. The name biodiesel is given by national biodiesel board which initiated the production of biodiesel in US from early 1990’s.

1.5.1 Importance of biodiesel production

There is a prompt decrease in fossil fuel sources in the world due to population growth and rapid industrialization. Also, the combustion of fossil fuels like coal and petrol generates greenhouse gas emissions, releases harmful pollutants which results in global warming and atmospheric pollution. The transportation sector is mainly based on fuels derived from petroleum. Climate can be greatly affected due to rapid increase of vehicles and can lead to environment instability. Hence, there is a great need for green fuel which can substitute fossil fuel sources.

The main advantages of biodiesel as alternative fuel are:

- It is biodegradable

- Low amount of overall emissions
- Emits little amount of toxic substances
- Can be derived from multiple feedstock
- High calorific value and excellent flash point
- Sulphur content is negligible

It can be used as an alternative to limited fossil fuels as a long term replacement there by reducing the crude oil imports. Biodiesel production can also generate employment in rural areas and can increase energy security. It can be used as blend with diesel normally or as a pure fuel for which engine modification would be necessary.

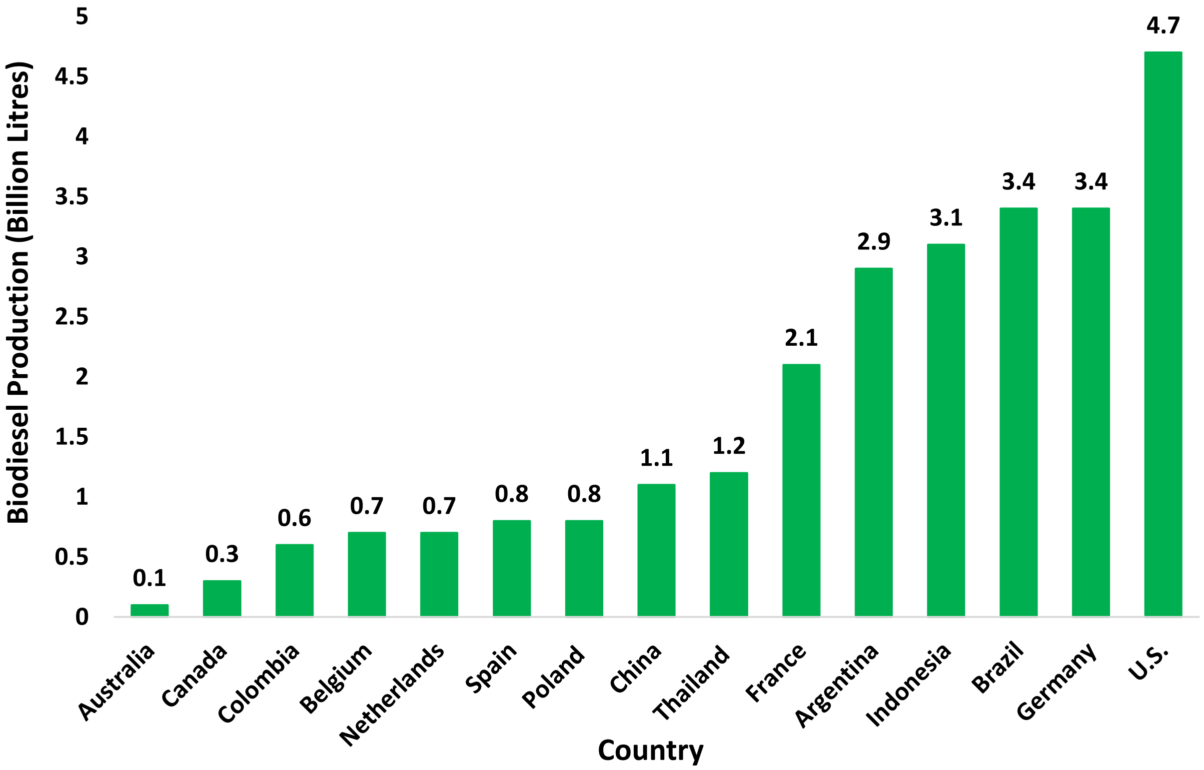


Figure 1.6 Country wise biodiesel production in 2014

(Source: www.statista.com, accessed on 20th October 2015)

Figure 1.6 shows country wise biodiesel production in 2014. United States is leading producer with 4.7 billion litres followed by Brazil and Germany. India produces a very little amount of biodiesel because of limited availability of feedstock. India imports large amount of edible oils to achieve food security in country. Using edible oils for biodiesel production will create food vs fuel problem.

Table 1.2 gives information about the major feedstock used for production of biodiesel in various countries. Most of the countries use palm oil, soybean oil and rapeseed oil for producing biodiesel however in India these oils are generally used for edible purposes. India is showing huge interest in non-edible oil sources for biodiesel production especially jatropha, pongamia, mahua and neem oils etc.

1.5.2 Why non-edible oils?

The price of biodiesel feedstock is high and accounts for more than 70% of total production cost which is hindering its production on a large scale. Hence, low cost feedstock such as non-edible oils can boost the economics of the process for materialistic production. At present, edible oils are being used as primary source for production of biodiesel which can affect the global market demand. It can also result in hike of edible oil prices and reduction of resources. On the other hand, non-edible oils are not used for human consumption and can be used as potential feedstocks. There are other advantages associated with non-edible oils which include wide variety of non-edible feedstocks available in large amounts throughout the world. They can be grown in any land with minimum costs. Also, less amount of water and fertilizers are required for their cultivation and can be grown in wide variety of climatic conditions. They also contain high amount of oil in seeds and kernels.

Nonetheless, as a major drawback, many non-edible plants have high amount of free fatty acids, which raises the biodiesel production cost.

Table 1.2 Country wise biodiesel production practices in the world

Sr. no.	**Country**	**Source of biodiesel**
1	USA	Soybean oil, mustard oil (under study)
2	Brazil	Soybean oil
3	Europe	Rapeseed oil and Sunflower oil
4	Nicaragua	Jatropha curcas oil
5	Spain	Animal fats, waste cooking oils and palm oil
6	Italy	Rapeseed, soyabean and palm oil

7	France	Rapeseed, palm oil and used cooking oil
8	Ireland	Animal fats, beef tallow and algal oils
9	Indonesia	Palm oil and jatropha curcas oil
10	Canada	Vegetable oils and animal fats
11	Australia	Beef tallow, used cooking oils, canola and mustard oil
12	Malaysia	Palm oil, jatropha curcas oil and algae
13	India	Jatropha curcas oil, pongamia oil, mahua oil, Neem oil etc. (non-edible oil).
14	Germany	Rapeseed oil
15	China	Guang pi

1.5.3 Fatty acid analysis of vegetable oils

Plant oils generally consists of glycerides of fatty acids. Fatty acids are composed of saturated and unsaturated aliphatic mono-carbon acids, whose structure consist of 4 to 24 carbon atoms. Triglycerides are the most common amongst plant oils. In these 3 hydroxyl groups (OH^-) of glycerol are replaced by fatty acids. Different oils have different composition of fatty acids. Physical and chemical properties of the plant oil is influenced by fatty acid composition. Jatropha oil generally consists of 20 % saturated fatty acid and remaining unsaturated fatty acid. Oleic acid ($C_{18}H_{34}O_2$) is the most abundant followed by linoleic acid ($C_{16}H_{32}O_2$), palmitic acid ($C_{18}H_{32}O_2$) and stearic acid ($C_{18}H_{36}O_2$) while composition of the oil is similar to other oil, which are generally used for edible purpose. According to the variety found in nature, 0.06 % to 10 % of the oil can be free fatty acids. Trace amount of sulfur and nitrogen may present up to 0.13 % and 0.11 %, respectively. Table 1.3 and 1.4 shows fatty acid composition of edible oils and non-edible oils, respectively.

1.5.4 Biodiesel production techniques

Oils and fats can be transformed into biodiesel in four ways: pyrolysis, dilution, micro-emulsions, transesterification. Transesterification is a method of converting triglycerides in oils

Table 1.3 Fatty acid composition of edible oils (Source: www.chempro.in, accessed on 4th April 2016)

Oil	**Lauric acid C12**	**Myristic acid C14**	**Palmitic acid C16**	**Stearic acid C18:0**	**Oleic acid C18:1**	**Linoleic acid C18:2**	**Linolenic acid C18:3**	**Arachidic acid C20**	**Any special fatty acid**
Coconut	44.0-52.0	13-19	8-11	1-3	5-8	0-1	……..	0-0.5	Palmitolic – 2.5
Corn	…….	0.2-1.0	8,0-12.0	2.8-5.0	19-49	34-62	……..	……..	……….
Palm	…….	0.5-2.0	32-45	2-7	38-52	5-11	……..	………	………….
Sesame	………..	………	7-9	4-5	40-50	35-45	……….	0.4-1.0	………….
Soyabean	……….	0.5	7-11	2-6	22-34	43-56	5-11	………	………….
Sunflower	………	………	3-6	1-3	14-35	44-75	………	0.6-4.0	Behenic – 0.8
Rapeseed	………	………..	1.5	0.4	22	14.2	6.8	………	Erucic- 47.0 Behenic – 2.0
Cottonseed	…….	0.4	20	2.0	35	42	…….	…….	……..
Peanut	……	……	6-9	3-6	52-60	13-27	…….	2-4	Lignoceric-1-3 Behenic-1-3

Table 1.4 Fatty acid composition of non-edible oils (Source: www.chempro.in, accessed on 4th April 2016)

Oil	Lauric Acid C12	Myristic Acid C14	Palmitic Acid C16	Stearic Acid C18:0	Oleic Acid C18:1	Linoleic Acid C18:2	Linolenic Acid C18:3	Arachidic Acid C20	Any special fatty acid
Castor	……..	…….	2.0	1.0	7.0	5.0	…….	……..	Ricinoleic - 86-90
Karanja	…….	…….	3.7-7.9	2.4-8.9	44.5-71.3	10.8-18.3	…….	2.2-4.7	Behenic - 4.2-5.3
Jatropha	……..	0.5-1.4	12.0-17.0	5.0-9.5	37-63	19-41	…….	0.3	Behenic - 0.6
Tobacco seed oil	…….	…….	9.6	6.3	21.7	55.6	……..	……	…….
Neem	…….	0.2-2.6	13.6-16.2	14.4-24.0	49-62	2.3-15.8	…….	0.8-3.4	…….
Mahua	……..	…….	20-25	20-25	41-51	10-14	…….	0.0-3.0	…….
Kokum	…….	0-1.2	2.5-5.3	52-56.4	39.4-41.7	1.7	……	…….	……

and fats into fatty acid methyl esters and has a potential to eliminate the high viscosity problem associated with feedstock. Non-edible oils can be converted into biodiesel through homogenously (acid or base) catalysed transesterification processes in one step or in two steps, heterogeneously catalysed transesterification processes in one step or in two steps, enzyme-catalysed transesterification processes and by supercritical and subcritical alcohol transesterification processes. Various process intensification technologies are developed for improving transesterification process reaction rate, FAME conversion and biodiesel yield. They include use of ultrasonic irradiation, use of microwave heating and use of co-solvent etc. Figure 1.7 shows different ways of biodiesel production.

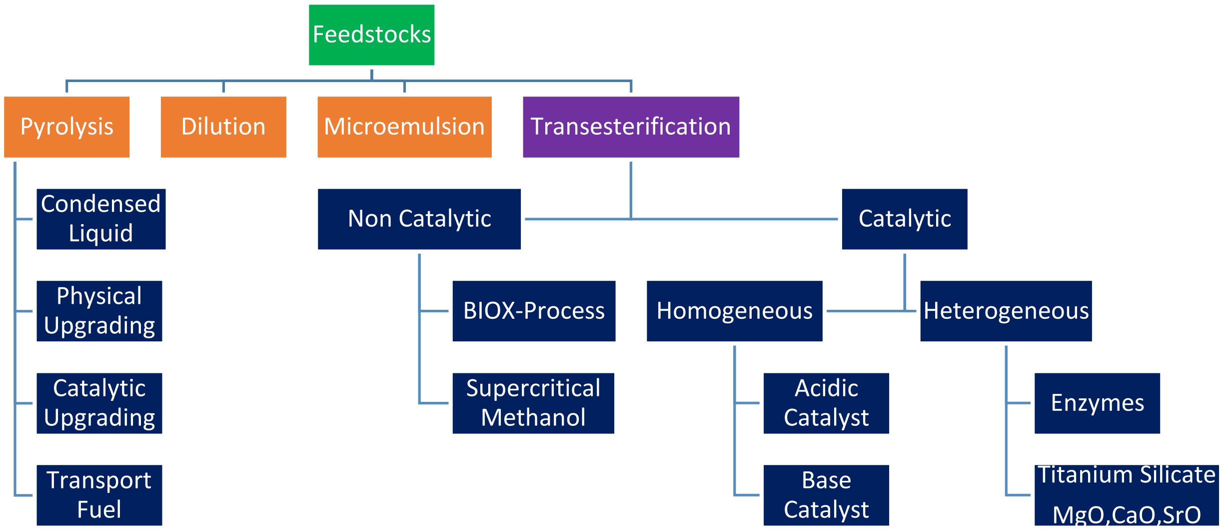


Figure 1.7 Different ways of biodiesel production (Source: Atabani et al., 2012)

1.5.5 Fuel properties of biodiesel

Biodiesel and diesel fuel properties have many similarities, and therefore, biodiesel is best rated as good replacement to diesel fuels. This is because the conversion of triglycerides into alkyl esters by the transesterification process decreases the viscosity by about one-eighth, decrease the molecular weight to one-third, and also enhance the volatility a bit. Biodiesel contains about one-tenth oxygen by weight, thereby enhancing process of combustion. The auto ignition quality of biofuel can be improved by the employment of tertiary fatty acid amides and amines without effecting the cold flow properties. Plugging and fouling of engines are the common problems that generally occur in cold environment. Both flash and fire points of biodiesel are generally 20 ^{0}C higher than commercially used motor fuels. Table 1.5 shows the fuel properties of biodiesel from different feedstocks.

Biodiesel can be used in its pure form or blend with diesel in different proportions to enhance fuel characteristics. As fuel properties of biodiesel are comparable with motor fuel, similar to that of diesel fuels, pure biodiesel can be used as engine fuel which needs only slight modifications of engine. There is no necessity for moderation in infrastructure for its storage. There is a reduction in emissions of toxic substances like particulate matter and carbon monoxide if used in diesel engines. Its negligible sulphur content, zero aromatic content and high oxygen content makes it a clean fuel. Ignition characteristics of fuel blended with biodiesel can be enhanced due to its high cetane index. As per new regulations on vehicle emissions, there is a need for very low sulphur content and high cetane index. Biodiesel will also help in improving the flash point that is required for safety.

B20 (a combination of 20 % biodiesel with 80 % diesel) has reported important environmental advantages in USA with a little enhancement of price for other customers. Department of transportation certifies pure biodiesel can be used as an alternative fuel in engines. There is significant reduction in particulate matter with the use of biodiesel in engines. Nitrous oxides emissions can be controlled by the use of catalyst. Carbon and carbon monoxide emissions were also observed to be lower.

Table 1.5 Properties of biodiesel from different oils (Source: Berchmans et al., 2008)

Sl.no.	**Feedstock**	**Kinematic viscosity (mm^2/s)**	**Cetane no.**	**Heating value (MJ/kg)**	**Cloud point (°C)**	**Pour point (°C)**	**Flash point (°C)**	**Specific gravity**
1	**Jatropha**	4.54	51	37.2	2	6	191	0.879
2	**Soyabean**	4.5	45	33.5	1	-7	178	0.884
3	**Palm**	5.73	62	33.5	13	-	163	0.880
4	**Pongamia**	3.4	-	38.3	-	7	188	0.876
5	**Sunflower**	4.63	49	33.5	1	–	184	0.861
6	**Mahua**	3.98	-	37	-	6	210	0.880

1.6 Status of Biodiesel in India

Government of India approved National Biofuel Policy (NBP) in December, 2009. It recommends use of biofuel as a substitute to fossil fuels and suggests complement 20 percent biofuel (biodiesel and bioethanol) mandate in India's total fuel supply by the end of 2017. Targets setup for biodiesel production in India by government to achieve blending ratios of 5, 10 and 20 percent in different phases with diesel by the end of 12th Five year plan. Table 1.6 shows biodiesel requirement for blending in different proportions in various years.

Table 1.6 Biodiesel requirement for blending (Source: www.planningcommission.nic.in)

Financial Year	Need for Diesel (MT)	Biodiesel requirement for blending (MT)		
		@ 5%	@10%	@20%
2005-2006	49.6	2.47	4.95	9.90
2006-2007	52.34	2.63	5.23	10.5
2011-2012	66.90	3.34	6.70	13.4

MT – Million Tonnes

The Government of India had launched the National Biodiesel Mission (NBM) identifying jatropha curcas oil as the most suitable non-edible oilseed for biodiesel production.

1.6.1 Developments in National Biodiesel Mission

- **April, 2003:** Proposal was made for accumulation of huge amount of land for jatropha farming. Proposal was also made for nursery development, seed gathering and construction of transesterification unit.

- **October, 2005:** Biodiesel purchase policy was advertised by GOI on January, 2006 stating that oil supplying companies can buy biodiesel from various outlets across the nation for blending purposes.

- **2008:** Self sustained phase. Proposed production of enough biodiesel for blending purpose by the end of 2012.

- **2010:** About half a million hectares were collected for jatropha farming and most of them were planted newly and requires time for growth.

- **Fiscal 2011/12:** Additional procurement of barren lands for jatropha farming was stopped although some oil marketing companies managed new plantations.
- **Fiscal 2012/13:** Biodiesel production from jatropha curcas oil still remained economically unreliable.
- **Fiscal 2013/14:** The production of biodiesel from alternative feedstocks was commercially viable option left with the farmers.
- **Present status:** Focus is shifting towards tree-borne oilseeds as a substitute to jatropha for producing biodiesel.

Currently, India has large capacity production plants which can produce more than 120 million liters of biodiesel from different sources. The produced biodiesel is supplied to automobile institutions for quality check and engine performance. Some amount of it is also sold to public and private organization to run buses. Little amount is used in generators for power backup.

Table 1.7 gives biodiesel production in India during the last six years. In 2010, the biodiesel production was 90 million liters which was increased to 135 million liters in 2015. There was no significant difference in biodiesel production from 2014 to 2015. There were no imports and exports made in last 6 years. Although production was increased by 50% in last 6 years but the 6 bio refineries in India are operating at an average capacity of 28.1% which is low indicating large scope for biodiesel production.

Table 1.7 Biodiesel production from multiple feedstock (Million liters) (Source: India Biofuels Annual, 2015)

Financial year	2010-11	2011-12	2012-13	2013-14	2014-15	2015-16	2016-17
Feedstock	45	39	43	44	46	49	46
Manufacture	90	101	116	120	129	135	138
Utilization	61	60	69	74	80	85	99
Remaining	39	41	47	46	49	50	39

1.6.2 Research and Development

The research on biodiesel is in premature stage, there is a necessity to implement diverse programs for its production, by product utilization and for testing engine performance. The main aim of R&D is to produce high quality feedstock to make biodiesel production, an efficient and cost effective technique. Biodiesel produced from various feedstocks may differ in the case of lubrication, composition and stability against oxygen. It is needed to carry out runs on biodiesel from all possible edible or non-edible oils available and prepare comparative values on fuel emissions, materials matchability and composition etc. Initiatives on toxic study of biodiesel from various sources should be taken by R&D centres before they are introduced. Procedure must be available to determine the amount of biodiesel in the blended fuel after adulteration.

The additional R&D matters which need attention are seed collection, resource assessment, preservation at low temperatures, employment of high yielding plants, oil quality, new agricultural techniques suitable for different climatic conditions, employing other catalysts like lipase and heterogeneous catalysts in biodiesel production, effective utilization of by-products apart from issues associated with biodiesel utilization as an additive and suitability for engine performance.

Priority for production of biodiesel from jatropha curcas has not progressed well in India as the economic viability of jatropha have proven to be unreliable. At present, there is no particular mandate for utilization of biodiesel in India. Focus should be shifted to other alternative sources like tree born oil seeds and a dedicated effort should be made for production of energy crops.

1.7 Motivation and Objectives

Biodiesel production and utilization is in the infancy stage in India. However there is a huge scope as most of non-edible feedstocks like jatropha curcas, karanja, neem, mahua, castor oils etc. are native to India. At present, most of the biodiesel produced is from batch process which incurs a huge production cost and processing. Also the batch process is time consuming and product quality is not uniform which makes it uneconomical. Therefore, there is a need to produce biodiesel in continuous process. But, operation in continuous process require large amount of feedstock, great detail of reaction information such as optimized process conditions in order to make the process economically viable. The main objective of present research work is to synthesize biodiesel using continuous ultrasonication from non-edible oils and also the optimization of the process parameters for maximum biodiesel yield.

The specific objectives are as follows:

1. A state of art of literature review on biodiesel production using edible and non-edible oils from ultrasonication process.
2. FAME production in batch process from soyabean and jatropha oils.
3. Experimental setup for biodiesel synthesis using continuous ultrasonication.
4. Design of experiments with response surface methodology using Design Expert.
5. Transesterification of esterified jatropha oil using continuous ultrasonication process.
6. Optimization of process parameters in biodiesel production from jatropha oil using continuous ultrasonication process.

CHAPTER 2

LITERATURE REVIEW

2.1 Feedstocks for FAME Production

Conventional feedstocks for biodiesel production are classified into four important groups.

1. Edible and non-edible plant oils
2. Waste vegetable oils (WVO) or used cooking oils
3. Animal fats
4. Algae

Edible oils are being used as primary source for production of fatty acid methyl esters (FAME). Based on the climatic conditions and fertility of land different types of edible oils are used in different countries which is reported in Table 1.2 of chapter 1. At present, biodiesel production from algae is gaining wide importance because of their unique advantages compared to other feedstocks. Waste materials like sewage can be used for algal growth and does not require land for their production and therefore available at a cheaper price. Oil content in algal oils is high and they can be grown within a short time. Animal fats such as beef tallow, lard, chicken fats and yellow grease are also used as feedstocks for biodiesel production. Although India produces edible oils in high amounts but it is not sufficient for domestic usage and imports approximately 50 % of edible oils in total.

In India, non-edible oils are used as primary feedstock for biodiesel production. More than 70 non-edible plant species are identified in India out of which one-third can be used for FAME production (Azam et al., 2005). Low sulphur and aromatic content, renewable nature, biodegradability makes them potential feedstocks while highly viscous nature, high carbon content and less volatile nature are some disadvantages associated with them.

2.1.1 Product characteristics from non-edible oils

Jatropha curcas, karanja, castor, mahua, rubber, neem and sea mango are the most common non-edible feedstocks used for biodiesel production. Table 2.1 gives a brief idea about the fuel advantages using different non-edible oils. All non-edible feedstocks lower the smoke emissions, CO and NO_x emissions where jatropha also increases the compression ratio of diesel engine.

Table 2.1 Fuel advantages from various non-edible oils. (Source: Ilic et al., 2012)

Oil plant	Fuel advantages
Jatropha Curcas	Lower particulate matter emission, high combustion efficiency.
Karanja	Lower nitrous oxides emission
Rubber	Smoke emissions are low
Mahua	Carbon monoxide, hydrocarbon, nitrous oxides emissions are low and reduced smoke tendency.
Neem	Lower smoke, carbon monoxide and nitrous oxides emissions

2.2 Transesterification

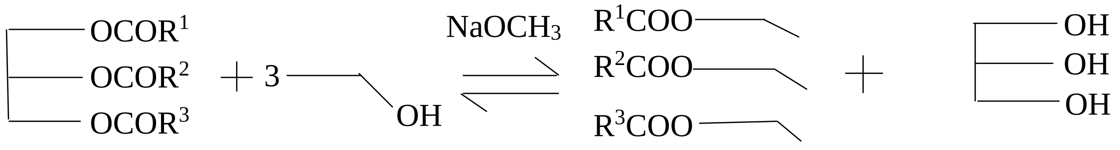
Transesterification of plant oils with alcohol results in production of fatty acid alkyl esters (FAAE). Transesterification reaction can be acid catalyzed, alkali catalyzed, enzyme catalyzed or non-catalyzed. Acid catalyzed transesterification requires a longer reaction time for a desired conversion. Alkali catalyzed transesterification is the most common method employed for FAAE production because of its shorter reaction time required for desired conversion. Alcohol is supplied in excess than required 3:1 stoichiometric ratio for the reaction completion.

Transesterification process involves reaction of triglycerides in feedstock with a short chain alcohol such as methanol or ethanol to produce FAAE and glycerol. The reaction takes place in the presence of strong base catalyst such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). Sodium methoxide ($NaOCH_3$) is also used as base catalyst. Heat is supplied at a constant rate for the reaction to proceed. Pretreatment is necessary for feedstocks having high free fatty acids (FFA). Esterification is carried out to reduce the FFA content to a very low value. Vegetable oils having FFA content < 2 wt. % do not require pretreatment. Generally non-edibles oils require pretreatment. During esterification step, free fatty acids in the feedstock reacts with alcohol (normally methanol) in the presence of sulphuric acid catalyst to produce fatty acid methyl esters and water.

$$R_1\text{-COOH} + CH_3OH \xleftrightarrow{\text{Sulphuric acid}} R_1\text{-COO-CH}_3 + H_2O \qquad \textbf{(2.1)}$$

FFA Methanol FAME Water

Scheme 1 Acid catalyzed esterification of Free Fatty Acids



(2.2)

Triglycerides Methanol FAME Glycerol

Scheme 2 Transesterification of Triglycerides with methanol

2.2.1 Operating variables

The important factors affecting biodiesel yield are:

- Alcohol: oil molar ratio
- Alcohol type
- Catalyst type and amount
- Reaction temperature and pressure
- Reaction time
- Intensity of mixing
- Amount of free fatty acids and water in oils.
- Effect of use of organic solvent

2.3 Transesterification Methods

2.3.1 Homogenously catalyzed transesterification process

Most widely used transesterification method which involves use of acid or base catalyst dissolved in methanol. The selection of type of catalyst depends on feedstock characteristics such as FFA content and composition. It can take place via one step or two step processes. One step process can be acid or base catalyzed while two step is both acid and base catalyzed.

2.3.1.1 One step process

High amount of FFA in non-edible oils limits the use of base catalyst. Free fatty acids present in feedstock reacts with base catalyst resulting in soap formation which reduces biodiesel yield. There will be a loss of catalyst amount and phase separation becomes difficult with soap formation. Base catalyzed transesterification is best suited with feedstocks having low FFA content. Sodium hydroxide, potassium hydroxide and sodium methoxide are the most commonly used base catalysts. Esterification of FFA is acid catalyzed which makes acid catalyzed transesterification a suitable process for biodiesel production from feedstocks having high FFA content in a single step. Acid catalyzed transesterification reaction rate is low and requires longer time to achieve desired conversion. Sulphuric acid (H_2SO_4) is generally used for acid catalyzed transesterification.

2.3.1.2 Two- step (acid/base) process

Two step process is most common method for production of biodiesel from non-edible oils. First step involves esterification of free fatty acids in the presence of acid catalyst which turns them into FAME. In the second step, transesterification of esterified oil is carried out in the presence of base catalyst. Two step process is more efficient and requires moderate reaction conditions and yield is high as compared to one step process. Two step process eliminates soap formation but the biodiesel production cost associated with it is higher.

Although transesterification using base catalysts have many advantages, there are also several problems associated with them. Base catalysts are hazardous and operating problems can occur while using them in continuous process. Moreover, washing and purification steps requires large amount of water which increases the overall production cost.

2.3.2 Effect of operating parameters

Methanol to oil molar ratio: Amount of methanol used in both esterification and transesterification is greater than the stoichiometric amount for completion of reaction. Esterification of FFA increases with increase in methanol: oil ratio resulting in a sharp decrease of acid value initially and remains constant with further increase due to the formation of water which stops the esterification reaction to proceed. Therefore, optimal molar ratio is necessary for the completion of esterification reaction. The optimal value is reported to be 6:1 by many researchers. During transesterification, the biodiesel yield increases with an increase in methanol: oil initially and remains constant with further increase. Using high amount of methanol results in decrease of biodiesel yield due to emulsification of glycerol with FAME, which makes it very difficult to separate them.

Catalyst concentration: Biodiesel yield increases with an increase in acid or base catalyst amount initially and reaches maximum and again decreases with an increase in concentration. Lower concentration of acid catalyst during esterification reaction does not decrease acid value to desired extent. Higher amount of acid catalyst gives darkened product. Similarly, lower base concentration during transesterification reaction gives very less yield whereas base concentration higher than optimum results in high amount of soap formation.

Reaction temperature: Research studies reveals that maximum ester yield is obtained in batch process when temperature ranges from 50-60 ^{0}C. It is due to the fact that methanolysis of triglycerides is much faster than saponification of FFA in the presence of base catalyst. Also, methanol starts evaporating at a temperature greater than 60 ^{0}C which results in excessive methanol loss thereby decreasing overall ester yield. To achieve desired yield excessive methanol should be used which increases the overall production cost. (Ilic et al., 2012)

2.4 Process Intensification Technologies

Process intensification involves application of new techniques to improve biodiesel yield, shorten the reaction time, decrease the production cost, and which simplify the process. Several methods have been studied to improve ester yield which includes application of ultrasonic irradiation, microwave heating, in-situ transesterification and co-solvent.

2.5 Ultrasonication

Ultrasonication involves application of high frequency sound waves normally greater than 20 kHz for agitation of particles present in a sample. Sound energy is a form of mechanical energy and has many applications when used at very high frequencies (20 kHz-200 kHz). High amount of energy is needed in processes involving the use of ultrasonic irradiation. Ultrasonic waves generate cavitation bubbles when it passes through a liquid phase. The generation of acoustic cavitation bubbles involves formation of tiny bubbles which grow in size within a short time. These tiny bubbles are a result of gaps generated which are filled with vapour from the liquid. These acoustic cavitation bubbles reaches critical size after which they breakdown to create micro jets. The collapse of these bubbles is almost an adiabatic process and the internal energy stored in these bubbles is released when they breakdown.

2.5.1 Sonochemistry

Sonochemistry is the study of mechanism of formation of acoustic cavitation bubbles upon ultrasonic irradiation which is responsible for enhancement of mass transfer rate between two immiscible liquids. No chemical effects are produced in the liquid mixture because of ultrasonication. It is due to the fact that the wavelength associated with ultrasonic frequencies is much longer than the bond length between atoms in a molecule. Therefore, sound waves cannot increase the internal energy of molecule directly. An explanation for the increase of internal energy is a result of cavitation. Cavitation involves formation, growth and collapse of bubbles in the liquid. The internal energy of these bubbles increases with size. Collapse of bubbles occurs after reaching a critical size results in micro jets of two liquids impinging into other phase at very high speed. Asymmetric breakdown of cavitation bubbles is responsible for generation of micro jets. Collapse of cavitation bubbles is near adiabatic process, internal energy stored in the bubbles is released in the form of heat which increases the temperature of liquid mixture. Collapse of bubbles can result in a local pressure of 2000 atm. and temperature can go upto 5000K. The entire mechanism is shown in Figure 2.1. Therefore, cavitation results in intense mixing of two immiscible liquids, thereby enhancing mass transfer rate.

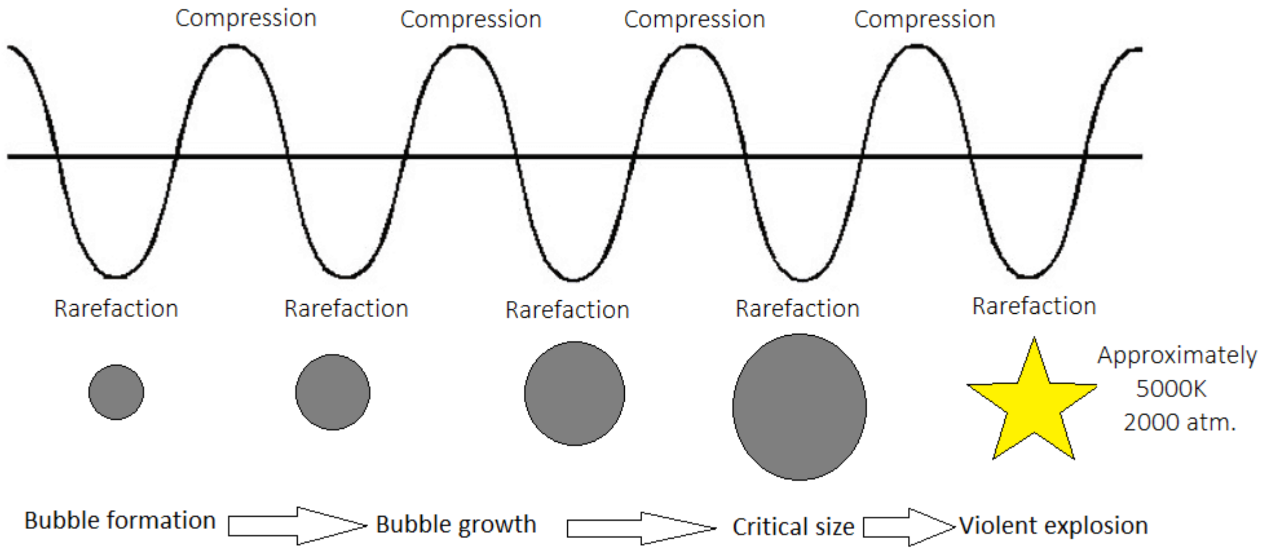


Figure 2.1 Cavitation Mechanism

2.5.2 Use of ultrasonication in batch biodiesel production

Ultrasonication is a recent, widely used technique in many applications, which involve multi-phase liquid systems such as transesterification process for biodiesel production. Transesterification involves oil and methanol which are immiscible. Use of ultrasonic irradiation enhances the mass transfer between the immiscible reactants thereby reducing the reaction time required to achieve a desired conversion. Also, employing process intensification techniques like ultrasonic irradiation improves biodiesel yield, requires mild reaction conditions and can support the use of heterogeneous catalysts for biodiesel production.

Figure 2.2 shows schematic diagram of biodiesel production in a batch process using ultrasonication. Alcohol and catalyst are mixed before feeding to the reactor. The mixture is added to biodiesel feedstock and is fed to the reactor. Ultrasonic probe provides the necessary energy for enhancing the mass transfer rate between oil phase and methanol phase which are immiscible. Research studies reveals ultrasonic assisted transesterification process using base catalyst is an efficient, time saving and cost effective method for biodiesel production. It provides highest biodiesel yield when compared with other processes.

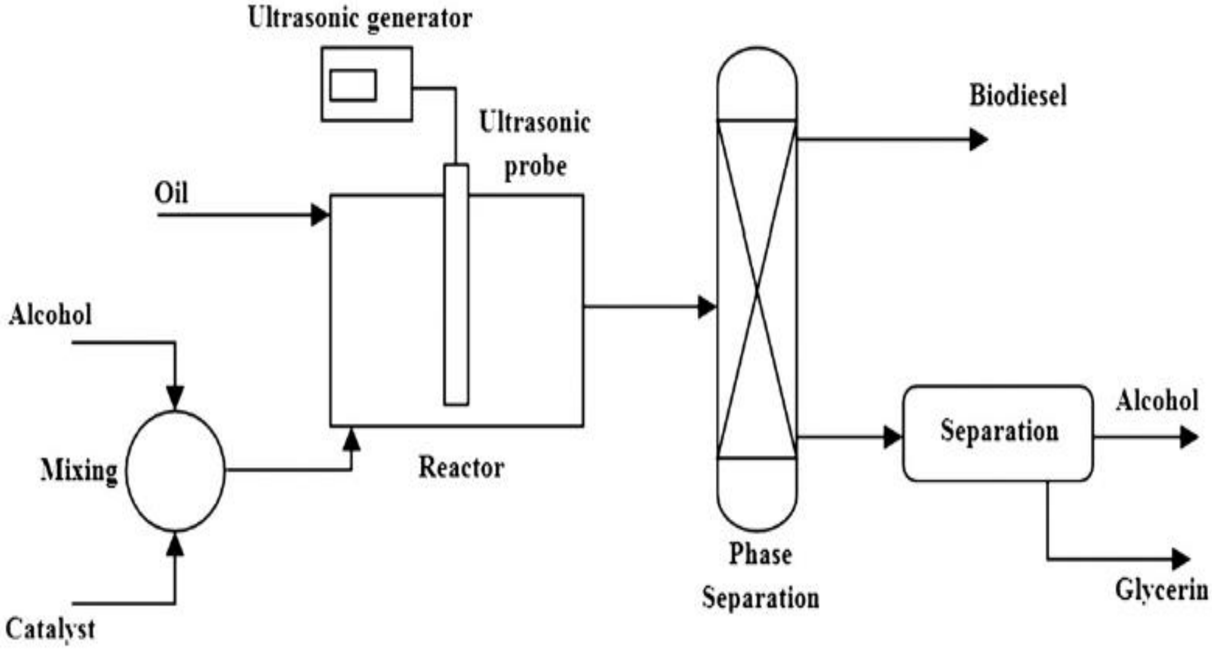


Figure 2.2 Schematic diagram of ultrasonic assisted batch biodiesel production (Source: Badday et al., 2012)

2.5.3 Use of ultrasonication in continuous biodiesel production

Batch process when compared to continuous process requires huge volume reactors for production of biodiesel on large scale. Batch processes are less efficient during start up and shut down conditions and involves high amount of labour which affect process economics. Although the biodiesel yield is less compared to batch process, it requires lesser time for production at a large scale. Because of the reasons stated above, in the recent years ultrasonic assisted biodiesel production in continuous process is receiving great attention.

Thanh et al. (2010) studied the design of pilot plant for the production of high quality biodiesel in two step continuous process. Experimental setup for continuous biodiesel production is shown in Figure 2.3. Transesterification of waste cooking oil (WCO) with methanol is carried out in the presence KOH using low-frequency ultrasonicator. Methanol and catalyst mixture and oil are pumped into first reactor at calculated flow rates to maintain a desired alcohol to oil molar ratio. The product mixture from the reactor is then sent to a separator where glycerol was removed from bottom. Top product was a mixture of biodiesel and unreacted oil having small amount of methanol. It is then fed to second reactor along with methanol and catalyst mixture to achieve high biodiesel yield. The product mixture from second reactor is again sent to separator where biodiesel is separated. The collected biodiesel is then washed and dried for removal of catalyst and methanol.

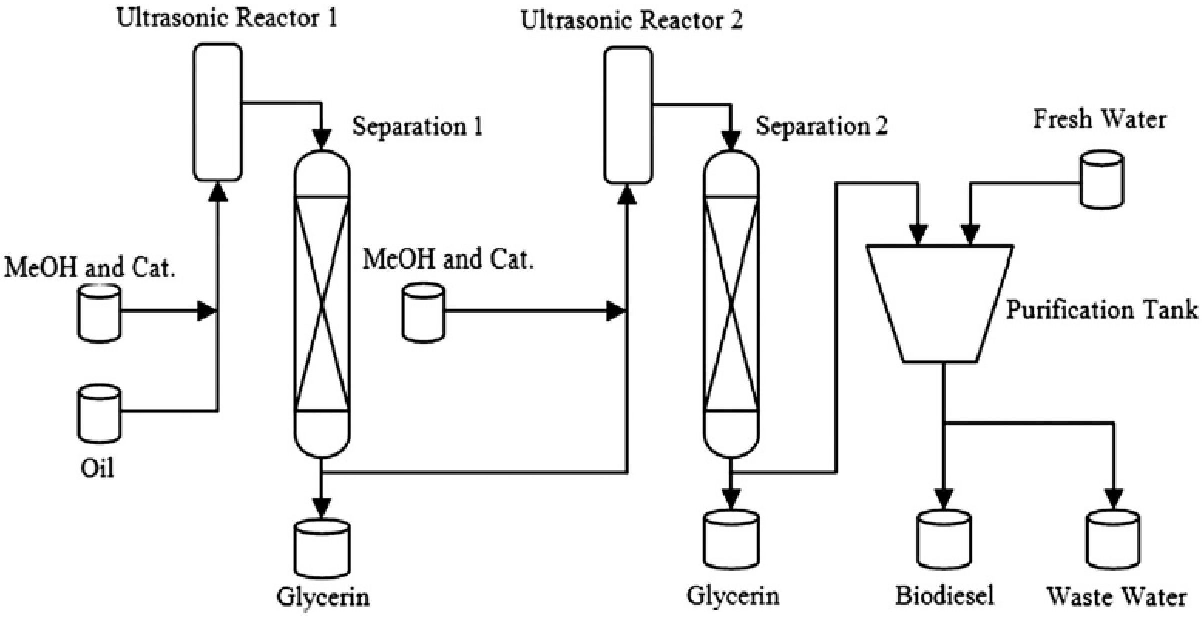


Figure 2.3 Flow diagram of two-step continuous process for biodiesel production (Source: Thanh et al., 2010)

Ji et al. (2006) prepared biodiesel using hydrodynamic cavitation and ultrasonic irradiation. Biodiesel production using ultrasonic irradiation in the presence of base catalyst resulted in high yield within shorter reaction time. Orthogonal experiments were performed to assess the effects of process parameters. Enhanced mass transfer rate between the two immiscible liquids was also observed using hydrodynamic cavitation. Both methods were shown to be cost effective, time saving and results in high biodiesel yield. Hydrodynamic cavitation can be used as promising method for biodiesel production at a large scale.

Stavarache et al. (2007) examined low frequency ultrasonic assisted transesterification process for production of fatty acid methyl esters from vegetable oils. Refined palm oil and cooking oil were considered for study. Transesterification reaction was carried out in two reactors having different volumes with different residence times. It was observed that high yield was attained with shorter residence time. It was noticed that alcohol to oil molar ratio and residence time mainly affects the biodiesel yield.

Cintas et al. (2010) investigated a new ultrasonic flow reactor and a pilot plant for reaction scale up. The developed ultrasonic flow reactor was applied in transesterification process involving soyabean oil and methanol as reactants and sodium methoxide as catalyst for FAME production. The reaction was carried out at a temperature of 45 ^{0}C for about 1 hour. This results in high amount of biodiesel yield. Employing a two- step procedure which involves mechanical stirring in first step and ultrasonic irradiation in second step also results in high amount of biodiesel yield with less energy consumption. This makes two-step process an energy efficient process when compared with one step process.

Kumar et al. (2012) carried out transesterification of jatropha curcas oil with different mixtures of methanol and ethanol at atmospheric conditions using ultrasonic irradiation. KOH was used as catalyst and 6:1 alcohol to oil molar ratio was taken for each experiment. Using a mixture of ethanol and methanol results in better solubility of oil and formation of both fatty acid ethyl and methyl esters. Ethanol was better solvent for oil but less reactive than methanol. The process was simple to operate and results in high biodiesel yield in a very short time as compared to conventional batch mixing.

Choudhury et al. (2013) investigated acid catalyzed transesterification process using ultrasonic irradiation. Optimization of process variables was studied and experiments were designed in Design Expert software using Box- Behnken Design (BBD). Esterification process is not affected by the use of ultrasonication but it enhances the transesterification reaction rate. It was observed that highest biodiesel yield was achieved at 70 ^{0}C, using 7: 1 methanol: oil ratio and 6 wt. % catalyst. The effect of each process parameter on biodiesel yield was difficult to interpret as they are interlinked with other process conditions. A little deviation from optimal values may lead to severe decrease in biodiesel yield. The study concluded that there will be no chemical effect of sonochemistry on transesterification process.

Thanh et al. (2013) studied transesterification of oils with alcohol in the presence of base catalyst using co-solvent process. Acetone was used as co-solvent. They investigated the effects of important process parameters such as amount of acetone used, catalyst concentration, reaction temperature and alcohol to oil molar ratio on biodiesel yield was investigated. The amount of FAME conversion at optimum conditions was greater than 98 % within half an hour. Same method was applied to different feedstocks such as canola, jatropha curcas, catfish and waste vegetable oil for biodiesel production. Biodiesel produced from all the feedstocks was quality tested and was found to satisfy Japanese biodiesel standards.

In another study, Choudhury et al. (2014) carried out ultrasonic assisted transesterification of jatropha curcas oil with methanol in the presence of chlorosulfonic acid catalyst. Chlorosulfonic acid can catalyze both esterification and transesterification reactions simultaneously. Also, chlorosulfonic acid improves kinetics of transesterification reaction when compared to other acid catalysts. Optimization of process parameters was studied and it was observed that mild reaction conditions are needed for high FAME yield when compared to conventional sulfuric acid catalyzed transesterification process. It was also noticed that change in Gibbs free energy was similar to that of sulfuric acid catalyzed transesterification process.

Hamze et al. (2015) examined the effects of various process parameters involved in biodiesel production from transesterification of waste cooking oil. BBD method was used for design of experiments. Experimental results revealed concentration of catalyst was the main factor. A FAME conversion of (99.38%) was achieved at optimal conditions. A second degree polynomial equation was developed that relates FAME conversion and biodiesel viscosity. Fuel properties found were matching with the international standards indicating high quality of biodiesel.

Mostafaei et al. (2015) evaluated transesterification of waste cooking oil (WCO) in continuous process. Statistical optimization of process parameters such as probe diameter, irradiation distance, amplitude, cycle ratio and flow rate were done using RSM. Central composite design

(CCD) was used for design of experiments. Results revealed that all the parameters taken were significant in determining biodiesel yield. The yield was found to be 91.6% at optimized conditions. An increase in biodiesel yield was noticed with an increase in amplitude and cycle ratio. The yield was also found increasing with an increase in probe diameter. Fuel properties of produced biodiesel were determined and met the ASTM and EN specifications for standard biodiesel.

An extensive literature is available on biodiesel production from non-edible oils. Various researchers have used different types of non-edible oils, catalysts and alcohols for production of biodiesel. Non-edible oils are cheap and can improve process economics. However, they need to be esterified as they contain high amount of FFA. Base catalyzed transesterification reaction was proven to be effective for biodiesel production. Ultrasonically driven transesterification process can be used for biodiesel production at industrial scale due to its simple application. Moreover, ultrasonic irradiation induces micro jets with high speeds which cause emulsification thereby enhancing the transesterification reaction rate. Continuous process was advantageous as it can be performed using small reactor. Block diagram of two-step biodiesel production process is shown in Figure 2.4.

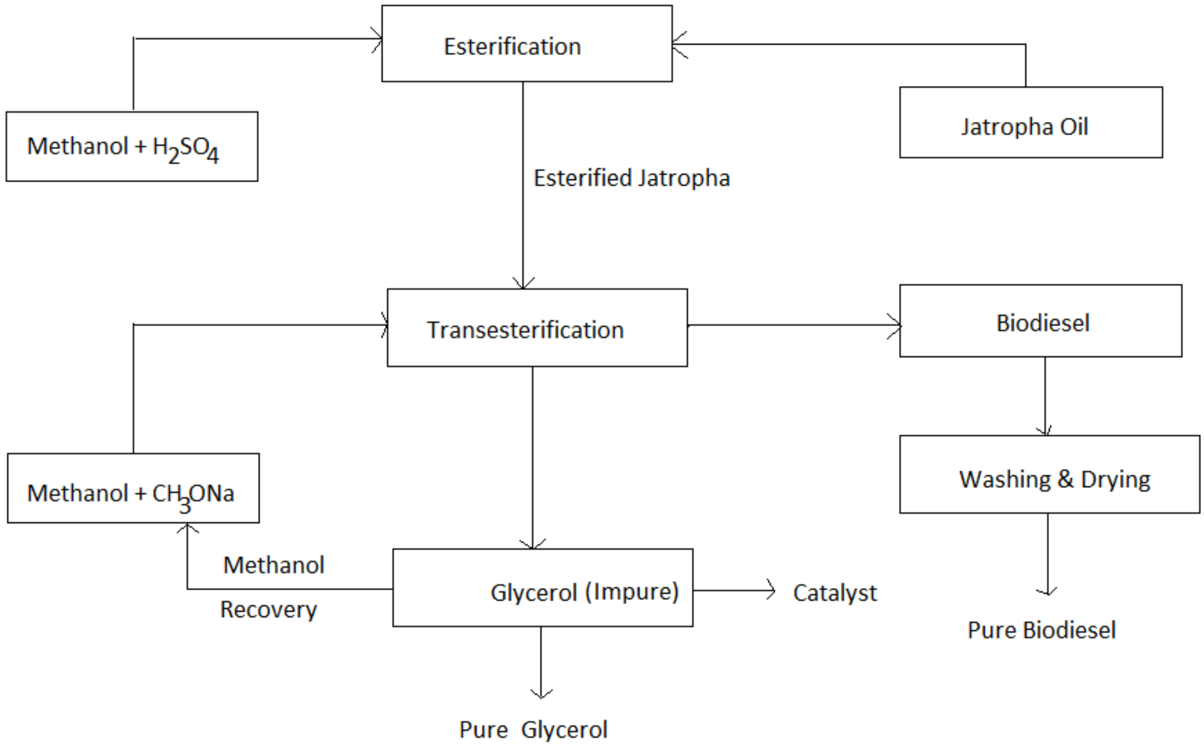


Figure 2.4 Block diagram of biodiesel production

CHAPTER 3

CHARACTERIZATION & BATCH PROCESS

3.1 Feedstock and Biodiesel Characterization

Estimation of the following physical and chemical properties is important related to biodiesel production.

- Density and specific gravity
- Kinematic viscosity
- Acid value
- Free fatty acids content
- Moisture content
- Flash point & fire point
- Cloud point & pour point

3.1.1 Density and specific gravity

Density and specific gravity were determined by using pycnometer. Mass of a known volume (generally 25ml) of empty bottle (w_1) was measured and then bottle was filled up to the 25 ml mark with feedstock or biodiesel and was weighed (w_2) using analytical balance. The bottle was then cleaned and dried in an oven and was filled up to mark by water and was weighed (w_3) again. The temperature at which measurements were taken was also noted (T ^{0}C).

$$\text{Density (T }^0\text{C)} = \frac{w_2 - w_1}{25} \quad \text{g/cm}^3 \tag{3.1}$$

$$\text{Specific gravity (T }^0\text{C)} = \frac{\text{Density of substance (t }^0\text{C)}}{\text{Density of water (4 }^0\text{C)}} \tag{3.2}$$

3.1.2 Kinematic viscosity

The kinematic viscosity of a fluid can be defined as a measure of its opposition to its deformation by shear stress or tensile stress. Redwood viscometer was used to determine the viscosity of feedstock and prepared biodiesel. It consists of a vertical cylinder with an orifice at the base centre closed by spherical ball. Cylinder was surrounded by a water bath which helps to maintain desired temperature at which liquid viscosity was measured. Liquid whose viscosity has to be measured was poured into the vertical cylinder and was heated till desired temperature was reached. The ball was then removed and the hot liquid was collected in a beaker. With the help of stopwatch the time required to collect 50mL of liquid was noted down.

The empirical equation relating kinematic viscosity and the time required to collect 50 ml of liquid is given below

$$\upsilon = At - B/t \tag{3.3}$$

where υ is the kinematic viscosity of the liquid, t is time needed to collect 50 ml of liquid in seconds. A is a constant and has a value 0.264 for $40 < t < 85$. For $85 < t < 2000$, the value of A is 0.247. B is constant with a value 190 for $40 < t < 85$ and has a value 65 for $85 < t < 2000$.

3.1.3 Acid value

Acid value is an important parameter, which gives an indication of the quality of feedstock and was determined by titration method. Acid value is defined as the amount of KOH required in milligrams to neutralize one gram of oil or fat. Ethanol was used as a solvent. A known amount of vegetable oil (0.5 g) was dissolved in 50 ml of ethanol and was titrated with 0.1 N standard KOH solution applying phenolphthalein indicator. Solvent without sample was also titrated in the same way.

$$\text{Acid value} = \frac{56.1 * V * N}{W} \tag{3.4}$$

where

V is difference in titration volume of standard KOH required for sample and blank in mL,

W is amount of sample taken in grams and

N is Normality of KOH solution.

3.1.4 Free fatty acid (FFA) value

Free fatty acid value is defined as the amount of oleic acid present in 100 grams of oil or fat except in coconut and palm oil. Free fatty acid value can be explained as a function of acid value as:

$$\text{Free fatty acid value} = \frac{\text{Acid value}}{1.99} \tag{3.5}$$

3.1.5 Flash and fire point

Flash point is the lowest temperature at which a volatile substance vaporizes to form an ignitable mixture with air upon application of an ignition source and ceases to burn upon its removal. Fire point is the lowest temperature at which the vapour produced by a given fuel continues to burn for at least 5 seconds upon application of test flame.

Pensky Marten closed cup flash point apparatus was used to measure flash point where cup filled with oil was closed with lid and heated at a low ramp rate with the help of heating plate. After a certain temperature the ignition source was inserted for every 1 ^{0}C rise and checked for flames. Closed cup apparatus gives a better approximation of flash point. Open cup apparatus was used to measure fire point where cup filled with oil was heated at a low ramp rate and ignition source was applied at regular intervals to determine the fire point.

3.1.6 Cloud and pour point

Cloud point refers to the temperature below which bio-wax in biodiesel and wax in diesel forms a cloudy appearance. It indicates the tendency of fuel to plug filters and orifices in engines in cold environments. The lowest temperature at which fuel appears semi solid and cease to flow is called pour point of fuel. Generally, a high pour point is associated with high paraffin content.

Cloud and pour point was measured with the help of cloud and pour point tester which has a stainless steel compartment insulated by polyurethane foam to minimize heat exchange with the surroundings. Compartment was provided with fully automated temperature controller, digital indicator with sensor and a cooling kit. In addition, a thermometer was also externally placed in the compartment to confirm the temperature readings. Sample was taken in test tube and was loaded in compartment and cooling was started. The temperature at which sample starts solidifying was noted down as cloud point. Sample is further cooled down and the temperature at which it becomes semisolid and seizes to flow was noted down as pour point.

3.2 Biodiesel Production in Batch Process

Transesterification of refined soyabean and esterified jatropha oils in batch process was carried out using both mixing and ultrasonication methods. Refined soyabean and crude jatropha oils were procured from a local market in Roorkee, India. Methanol and sodium methoxide of analytical grade were used as reactant and catalyst respectively and were purchased from Sigma-Aldrich Company.

3.2.1 Procedure for batch mixing

Transesterification of soyabean oil was carried out in a 500 mL three necked glass flask equipped with thermometer, reflux condenser and a sampling port. The flask was dipped in silicone oil medium which controls the temperature in flask. Magnetic beads were placed in both flask and silicone oil and the set up was placed on heating mantle of stirrer which provides agitation. Constant agitation speed was maintained at 250 RPM throughout the experiment. Figure 3.1 shows schematic diagram of experimental setup.

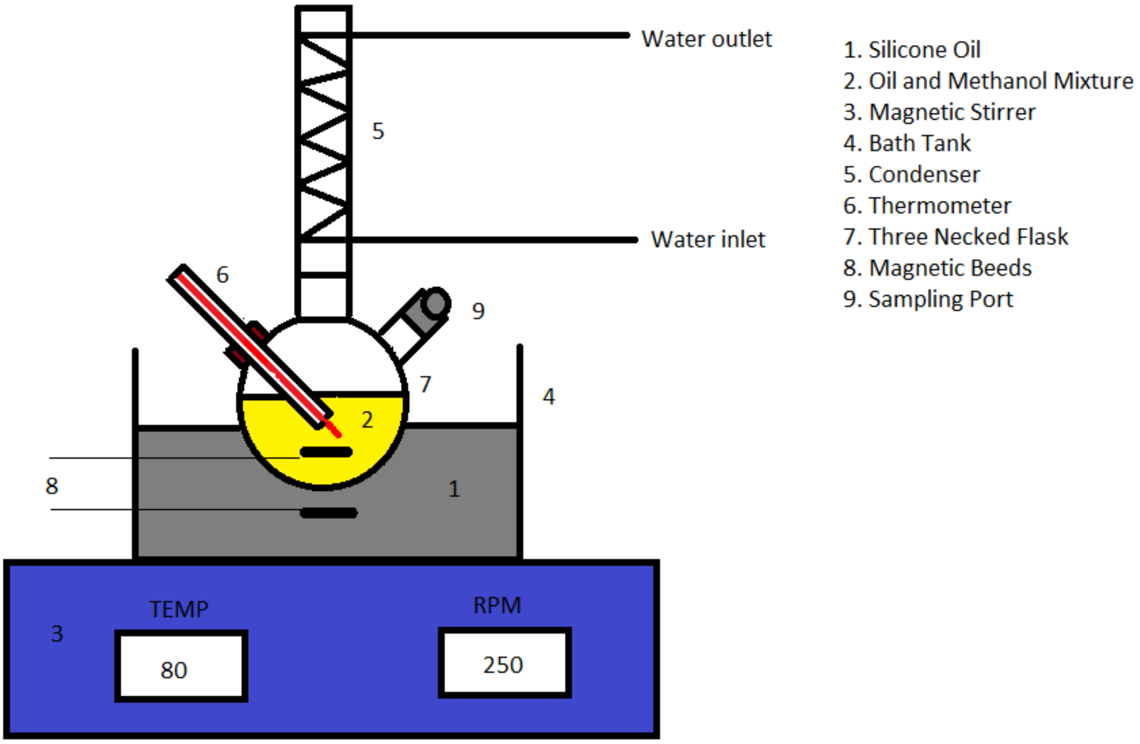


Figure 3.1 Schematic diagram of experimental batch setup

Refined soyabean oil has low FFA value, so esterification was not necessary. A known amount of soyabean oil (about 200 mL) was taken in three necked flask setup and was preheated to a desired temperature (60 ^{0}C). A calculated amount of sodium methoxide 1 wt. % was mixed with 6:1 molar ratio of methanol to oil. When the oil reaches desired temperature, the alcohol and catalyst mixture was poured into the flask and the temperature suddenly drops but was maintained at desired level by heating. The batch operation was carried out for 3 hours. The liquid mixture in flask was collected and poured into separating funnel, as shown in Figure 3.2. The liquid mixture separates into two phases in the funnel. The top product was biodiesel having small amount of unreacted methanol and the bottom product was glycerol containing unreacted methanol and impurities. The bottom product was separated and the top product was collected in another vessel. Purification involves washing and drying of collected biodiesel.

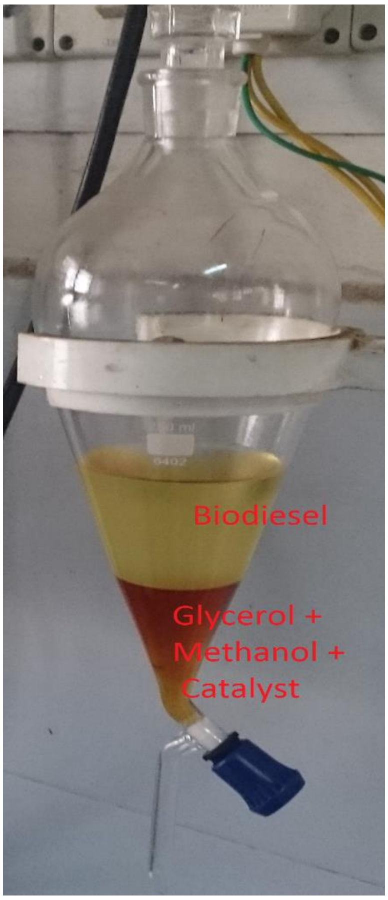


Figure 3.2 Phase separation of liquid mixture

3.2.2 Procedure for batch ultrasonication

Transesterification of refined soyabean oil with methanol was carried out in the presence of sodium methoxide catalyst using ultrasonicator processor UP 400S bought from Hielscher Company which is shown in Figure 3.3. A known amount of soyabean oil (200 mL) was taken in a beaker and methanol + $NaOCH_3$ mixture was added to it. A 6:1 methanol to oil molar ratio and 1wt. % of catalyst w.r.t oil was used. The beaker was then placed inside the ultrasonicator setup where probe was immersed half way in the oil and alcohol mixture. Ultrasonicator was then switched off and temperature was noted down continuously with the help of temperature sensor. The reaction was carried out at a temperature below 60 ^{0}C. The reaction was carried out setting both amplitude and pulse ratio at 70 % for 15 minutes and the ultrasonicator is switched off. The product mixture was allowed to cool down to room temperature and was poured into separating funnel where it gets separated into two phases. The upper phase was biodiesel containing small amount of alcohol and lower phase was glycerol containing unreacted methanol and catalyst. Separation and washing was carried out for purification of biodiesel.

Figure 3.3 Experimental setup for batch ultrasonication

3.2.3 Gas chromatography analysis

To calculate the amount of FAME conversion, the prepared biodiesel was analyzed using gas chromatography (GC) technique. Methyl heptadeconate, 99% pure, was used as internal standard. The procedure for GC analysis is given below:

- Prepared GC internal standard solution by dissolving methyl heptadeconate in n-heptane. The concentration of methyl heptadeconate in n-heptane is approximately 10mg/mL.
- 200 µL of biodiesel sample was taken in 10 mL vials.
- 2 mL of prepared internal standard solution was added to the biodiesel sample taken.
- 1 µL of the above solution was injected into gas chromatography with the help of micro syringe.
- The micro syringe was cleaned at least 10 times before injecting the sample into gas chromatography.
- Gas chromatograph used was Michro 9100 from Netel Company, and the conditions used for GC analysis are shown in Table 3.1.

Table 3.1 Gas chromatograph conditions

Parameters in GC	**Value**
Inject temperature	230 ^{0}C
Oven program initial temperature	180 ^{0}C
Oven program final temperature	240 ^{0}C
Hold time 1	0 minutes
Hold time 2	6 minutes
Injection volume	1 µL
Ramp 1	4 ^{0}C
Column	Optima Wax (30 m × 250 µm × 0.25µm) fused silica capillary column
Carrier Gas	Nitrogen
FID Temperature	240 °C
Detector	Flame Ionization Detector
Gas Flow	3.0 mL/minute

CHAPTER 4

EXPERIMENTAL SETUP AND METHODOLOGY

Biodiesel was produced from jatropha which is a non-edible oil. Jatropha contain high amount of free fatty acid value and require pre-treatment before transesterification. Esterification of jatropha was carried out in the presence of sulphuric acid in order to remove free fatty acids. In the present work, biodiesel synthesis was carried out in following steps:

- Degumming and esterification of non-edible oil,
- Transesterification of esterified non-edible oil,
- Refining of produced biodiesel, and
- Quality testing of biodiesel with EN biodiesel standards.

4.1 Experimental Procedure

4.1.1 Materials

Jatropha curcas oil was purchased from a local market. The acid value of jatropha was determined by titration method using 0.1 N standard KOH solution. Free fatty acid value of jatropha was calculated from acid value. FFA value was higher than 2 wt. %, therefore the oil was esterified to remove free fatty acids using acid catalyst. Sulphuric acid used in acid catalyzed esterification process was purchased from Thermo Fischer Scientific Company. Methanol and sodium methoxide of analytical grade used in transesterification reaction were purchased from Sigma-Aldrich Company.

4.1.2 Reaction conditions

Transesterification reactions were carried out at 35-40 ^{0}C temperature using sodium methoxide as catalyst. Transesterification reactions were carried out at varying ultrasonic amplitude, pulse ratio and at different flow rates. All the experiments designed were carried out using 1 wt. % catalyst concentration and 6:1 alcohol: oil molar ratio. Amplitude was varied from a minimum of 20 % to maximum of 100 % whereas total flow rate was varied from 3 to 7 mL/min. Pulse ratio was varied from a minimum of 20 % to maximum of 100 %.

4.1.3 Apparatus

Continuous transesterification reaction was carried out using ultrasonic irradiation in a stainless steel reactor of volume 30 mL approximately having orifices for feed inflow and product outflow. Orifices were also available for water circulation around the reactor in order to condense vaporized methanol and to maintain temperature inside the reactor. Temperature was measured with the help of temperature sensor. Calibration of temperature sensor was done with the help of thermometer and hot water. The ultrasonic processor UP 400S purchased from Hielscher Ultrasound Technology Company was used as a source of ultrasonic irradiation for assisting biodiesel production. The processor was operated at a frequency of 24 kHz with a maximum power of 400 W. A sonicator probe made up of titanium having a diameter 22 mm approximately was used for irradiation, shown in Figure 4.1. Sound protection box facility was available with the ultrasonicator. Three containers were used one for jatropha oil, one for alcohol and catalyst mixture and other for produced biodiesel. Two peristaltic pumps were used one for pumping jatropha and other for pumping mixture of alcohol and catalyst. Calibration of pumps was done using respective fluids. A T-joint was used where the reactants come into contact and were mixed before fed to the reactor. The schematic diagram and experimental setup are shown in Figure 4.2 and Figure 4.3 respectively.

Reactor volume - 30 mL

Probe dimensions:
Length- 100 mm
Diameter- 22 mm

Figure 4.1 Reactor and probe dimensions

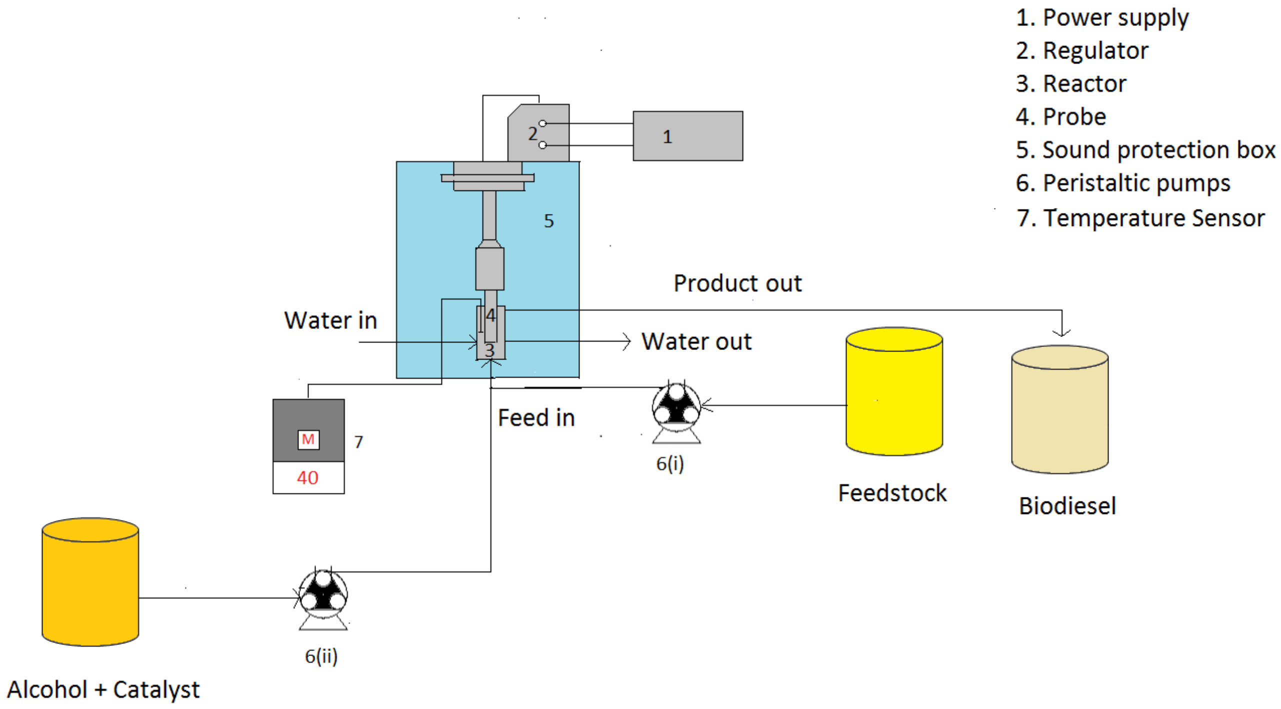


Figure 4.2 Schematic diagram of biodiesel production using continuous ultrasonication

Figure 4.3 Experimental setup of biodiesel production using continuous ultrasonication

4.1.4 Esterification

Degumming of jatropha oil is carried out before esterification. Crude jatropha oil is washed with water at 50 ^{0}C for 1 hour to remove water soluble impurities. Washed jatropha oil is separated from water and is esterified. During esterification process, a known amount of jatropha oil (200 g) was taken in three necked flask of volume 500 mL and was heated to 60 ^{0}C. 40 g of methanol and 10 g of sulphuric acid solution was added to flask and stirred at a constant speed for three hours maintaining the temperature at 60 ^{0}C. 2 mL samples were collected at 5, 10, 15, 30, 60, 90, 120, 180 minutes. The product mixture was then poured in a separating funnel where it gets separated into two phases. The upper phase was esterified jatropha oil containing small amount of methanol and the lower phase was water containing glycerol, unreacted methanol and catalyst. Upper layer was separated, washed with water for 2-3 times and was tested for FFA which turns out to be less than 0.5%. The collected 2 mL samples were also tested for FFA to know the decrease in free fatty acid content with time.

4.1.5 Transesterification

Esterified jatropha oil and alcohol (methanol) + catalyst (sodium methoxide) were pumped at calculated flow rates with the help of peristaltic pumps to achieve a desired total flow rate and 6:1 alcohol: oil molar ratio. The ultrasonication apparatus amplitude and pulse were adjusted according to the designed experiment. Oil and alcohol were mixed using a T-joint and was fed to the reactor where transesterification reactions were carried out at 35-40^{0}C under ultrasonication. When the first drop comes out of reactor the ultrasonicator was switched on. Digital temperature sensor was also switched on simultaneously. When temperature inside the reactor reaches 40 ^{0}C, stopwatch was switched on and product mixture was collected after processing of one reactor volume. For uniform product quality, temperature inside the reactor was maintained at 35-40 ^{0}C by circulating water. Transesterification reaction was carried out till 40 mL of product was collected. The apparatus was then switched off and the product mixture was transferred to a separating funnel.

4.1.6 Cleaning of apparatus

Ultrasonicator was allowed to cool down to room temperature. The pipes were removed from the setup. There was a deposition of catalyst particles in methanol inlet pipe which should be removed otherwise fouling of pipeline occurs. Reactor was dismantled from the setup and was opened for cleaning. Little amount of glycerol was deposited at the bottom. Cleaning of reactor and ultrasonicator probe was done using acetone. The reactor was then allowed for drying at room temperature.

4.1.7 Washing and drying of biodiesel

The product mixture separates into two phases when poured in separating funnel. Biodiesel was collected from top and contains impurities like unreacted jatropha and small amount of methanol. Glycerol was collected from bottom which contain unreacted methanol and catalyst. Washing of biodiesel was carried out with water for removal of impurities. An equal amount of water was mixed with biodiesel and was heated at 50 ^{0}C for 1 hour and poured into a separating funnel. Milky white colour was appeared due to soap formation and it was allowed to stand for 12-24 hrs. Impurities settle down in water phase and biodiesel was obtained at top. Washing was done until a clear layer of water appears at the bottom. Biodiesel collected from last washing looks hazy and was heated at a temperature of 130 ^{0}C for 3-4 hours for removal of moisture. This results in pure biodiesel which was clear and light yellow in colour.

4.1.8 Gas chromatograph analysis

GC analysis was carried out using Michro9100 GC manufactured by NETEL Company. The steps involved in GC analysis were already discussed in chapter 4. Precaution to be taken that no water should be present in the sample used for GC analysis, which may destroy the column used in GC. FAME conversion, volume yield and biodiesel yield were calculated using the following equations.

$$\%\ \text{FAME conversion} = \frac{(\text{Total area under FAME peaks - Area under IS peak})}{\text{Area under IS peak}} * \text{Concentration of IS} * \frac{\text{Volume of IS solution taken}}{\text{Weight of sample taken}} * \text{Purity of IS} * 100 \qquad \textbf{(4.1)}$$

$$\text{Volume yield} = \frac{\text{Amount of biodiesel obtained}}{\text{Amount of oil fed to reactor}} * 100 \qquad \textbf{(4.2)}$$

$$\%\ \text{Biodiesel yield} = \frac{\%\ \text{FAME conversion} * \text{Volume yield}}{100} \qquad \textbf{(4.3)}$$

4.2 Design of Experiments

Biodiesel yield from non-edible oils under continuous ultrasonication depends on several parameters. Many researchers studied the effect of temperature, catalyst and its weight percent, alcohol to oil molar ratio on biodiesel yield in batch process. It was reported by many researchers that a yield of 93-95 % was achieved in batch process at 45 ^{0}C temperature, when 6:1 alcohol to oil molar ratio and 1 wt. % catalyst is taken.

In the present study, three different parameters, amplitude, pulse ratio and total flow rate were considered in designing experiments. The experiments were designed in Design Expert 9 software using Response Surface Methodology (RSM). The Central Composite Design (CCD) model with three independent parameters predicts 20 experiments with 6 replicates at the centre and 14 factorial experiments.

The settings for the three independent variables is listed in the Table 5.1. Five levels were taken for each variable and alpha value was set at 2, amplitude and pulse ratio were varied from 20 to 100 % whereas total flow rate was varied from 3 to 7 mL/min. All the factors considered were numeric. A 6:1 methanol to oil molar ratio and 1 wt. % of sodium methoxide catalyst was taken for all the experiments.

Table 4.1 Settings of operating parameters

Variables	**Levels**				
	-2	-1	0	1	2
Amplitude	20	40	60	80	100
Pulse ratio	20	40	60	80	100
Flow rate	3	4	5	6	7

Central Composite Experimental Design (CCED) was a quadratic regression model which considers all effects of linear and quadratic terms and also includes the two level interaction between all parameters. Randomization of experiments was done to avoid bias or prejudice.

CHAPTER 5

RESULTS & DISCUSSION

In this chapter physical and chemical properties of refined soyabean oil and crude jatropha have been studied. Acid value was calculated to determine the FFA content in the feedstock. The amount of FFA content was greater than 2 wt. %, therefore pretreatment of feedstock is necessary in order to avoid high amount of soap formation. Physical and chemical properties such as specific gravity, density, kinematic viscosity, flash and fire points, cloud and pour points of biodiesel produced were also determined.

5.1 Physical and Chemical Properties of Feedstock

Characterization of refined soyabean and jatropha oils were carried out to determine density, acid value, kinematic viscosity, and the results are reported in Table 5.1.

Table 5.1 Characterization of feedstock

Property	Soyabean oil	Jatropha oil
Density (33 ^{0}C)	0.9172 g/cm^3	0.9131 g/cm^3
Specific gravity (33 ^{0}C/ 33 ^{0}C)	0.9220	0.9180
Kinematic viscosity (40 ^{0}C)	32.11 cSt	44.31 cSt
Acid value	2.06	19.07
Free fatty acid content	1.03	9.583

Table 5.1 shows that density of soyabean oil was little higher than jatropha oil. Kinematic viscosity of crude jatropha was high as compared to soyabean oil which interprets that jatropha was more viscous than soyabean oil. The acid value of soyabean oil was low and therefore no pretreatment was necessary whereas the acid value of jatropha oil is 19.07 and the FFA content was 9.583 which was very high as compared to 1.035 of soyabean oil. Therefore crude jatropha was esterified using methanol in the presence of acid catalyst to reduce FFA content. Samples were taken at regular intervals during esterification to determine the reduction of FFA content

with time and is shown in Figure 5.1. FFA content was greatly reduced at the start of esterification reaction and it slows down with the progression of time. By the end of three hours, FFA content was reduced from 9.583 to 0.648.

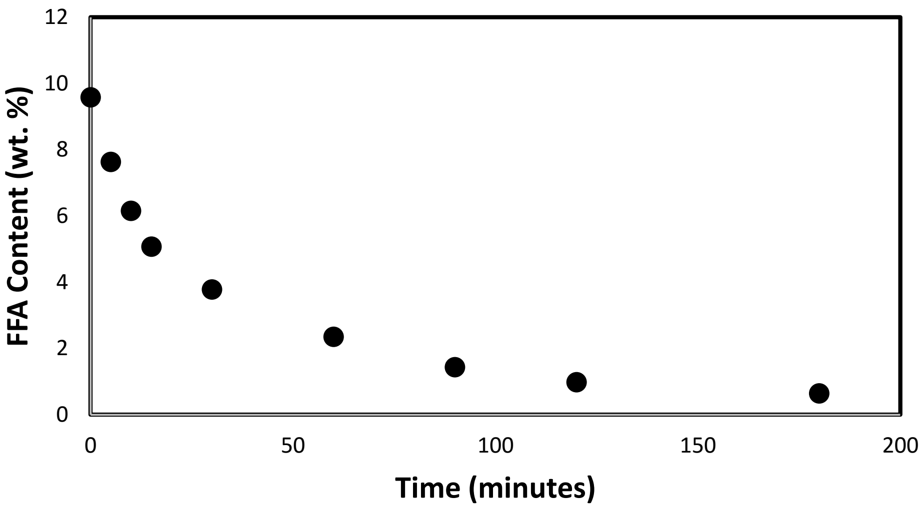


Figure 5.1 Variation of FFA content with time during esterification

5.2 Biodiesel Production in Batch Process

Biodiesel produced in batch process was characterized using GC analysis to determine the amount of FAME conversion. Table 5.2 shows the amount of FAME conversion, volume yield and biodiesel yield for refined soyabean oil and jatropha oil using batch mixing and batch ultrasonication.

Table 5.2 Biodiesel yield using batch mixing and ultrasonication

Feedstock	Process	FAME Conversion (%)	Volume Yield (%)	Biodiesel Yield (%)
Soyabean	Batch Mixing (3 hr.)	92.85	96.2	89.32
	Batch Ultrasonication (15 min)	94.94	95.4	90.57
Jatropha	Batch Mixing (3 hr.)	92.02	96.6	88.89
	Batch Ultrasonication (15 min)	93.83	95.6	89.70

% FAME conversion using soyabean oil was slightly higher than with jatropha oil. The amount of FAME conversion was high with batch ultrasonication process than with mixing process for both the feedstocks. FAME conversion was determined to be greater than 90 % with both the oils using either mixing or ultrasonication. Volume yield was determined to be little higher in mixing process than using ultrasonication which was due to the fact that reaction was carried out for much longer time in mixing process. Volume yield also depends on the amount of FFA content in the feedstock. Higher the amount of FFA content lesser will be the yield. The FFA content in esterified jatropha oil was less compared to soyabean oil which results in higher volume yield. Volume yield for all the cases was estimated to be more than 95%. Biodiesel yield can be calculated from FAME conversion and volume yield. The yields were calculated to be high in each case and the highest yield was achieved in the case of soyabean oil using batch ultrasonication process whose value was 90.57 %.

Physical and chemical properties of biodiesel such as density, specific gravity, kinematic viscosity, flash and fire point, cloud and pour point, obtained using batch ultrasonication were studied and are reported in Table 5.3.

Table 5.3 Physical and chemical properties of biodiesel from batch ultrasonication

Fuel Property	**Standard Biodiesel (EN14214)**	**Biodiesel from ultrasonication**	
		From soyabean oil	**From jatropha oil**
Density @ 15.5 ^{0}C, kg/m^3	860 - 900	873	866
Specific gravity @ 15.5 ^{0}C	0.860 - 0.9	0.873	0.866
Kinematic viscosity @ 40 ^{0}C, mm^2/s	3.5 - 5.0	4.3	4.5
Flash point , ^{0}C	> 101	131	135
Fire point, ^{0}C	110 - 205	152	157
Cloud point, ^{0}C	Location and season dependent	-2	0
Pour point, ^{0}C	Location and season dependent	-5	-3

The properties of produced biodiesel were compared with properties of standard biodiesel. Density and kinematic viscosity of biodiesel produced from jatropha are lower than biodiesel produced from soyabean oil. All the properties fall in the range of standard biodiesel, therefore the biodiesel can be used for blending purposes.

5.3 Biodiesel Production in Continuous Process

Various parameters such as amount of alcohol, alcohol to oil molar ratio, catalyst, catalyst concentration, amplitude, pulse ratio and total flowrate were involved during biodiesel production using continuous ultrasonication. Temperature also plays an important role in determining biodiesel yield. In the present work, transesterification of vegetable oil, a 6:1 methanol: oil molar ratio was taken. Sodium methoxide with 1 wt. % concentration was used as catalyst and temperature was maintained at 35- 40 ^{0}C for all experiments. Amplitude and pulse ratio was varied from 20% to 100% and total flow rate was varied from 3 to 7 mL/min at five levels, shown in Table 4.1. A total of 20 experiments were designed using CCD method in RSM taking alpha as 2.

All experiments designed were carried out using jatropha curcas oil and the results are shown in Table 5.4. It was noticed that highest FAME conversion was obtained at 80 % amplitude, 80 % pulse ratio and 4 mL/min total flowrate. FAME conversion at these operating conditions was calculated to be 77.21 %. Lowest FAME conversion was 53.83 % which was obtained at 60 % amplitude, 60 % pulse ratio and 7 mL/min total flowrate. Predicted values of FAME conversion using quadratic model were nearly same as experimental values and are shown in Figure 5.2. It was noticed that FAME conversion increases with an increase in amplitude initially, reaches maximum and almost remains same with further increase in amplitude. It was observed that with an increase in pulse ratio there was an increase in FAME conversion. Also, FAME conversion decreases with an increase in flowrate.

Biodiesel yield was maximum at 80 % amplitude, 80 % pulse ratio and 4 mL/min total flowrate and was determined to be 70.82 %. Minimum biodiesel yield was calculated to be 49.79 % at 60 % amplitude, 20 % pulse ratio and 5 mL/min total flowrate. Predicted values of biodiesel yield using quadratic model were matching with the experimental values and are shown in Figure 5.3. A little change in biodiesel yield was observed with a change in amplitude. Biodiesel yield was observed to increase with an increase in pulse ratio, approaches maximum and decreases thereafter. It was also noticed that biodiesel yield increases with a decrease in flowrate, due to less residence time in the reactor.

Table 5.4 FAME conversion and biodiesel yield at different reaction conditions

Run	Amplitude (%)	Pulse (%)	Total flowrate (mL/min)	FAME Conversion (%)		Biodiesel Yield (%)	
	A	B	C	Experimental	Predicted	Experimental	Predicted
1	40	80	6	60.46	60.82	54.92	54.59
2	80	40	4	63.76	63.92	58.61	58.68
3	40	40	4	66.52	66.59	61.42	61.59
4	40	40	6	55.21	55.48	57.26	56.95
5	100	60	5	68.37	68.15	60.99	61.12
6	80	80	6	69.14	69.59	59.25	58.82
7	60	60	5	69.99	69.80	65.34	65.19
8	60	60	5	69.85	69.80	64.93	65.19
9	80	40	6	57.32	57.41	53.01	52.81
10	40	80	4	72.87	73.30	65.44	65.38
11	60	60	5	70.05	69.80	65.55	65.19
12	60	60	5	69.81	69.80	64.90	65.19
13	60	60	3	72.70	72.50	68.07	67.83
14	60	100	5	74.30	73.82	59.34	59.60
15	60	60	5	69.92	69.80	65.21	65.19
16	60	20	5	54.97	54.93	49.79	49.79
17	20	60	5	62.36	62.06	59.66	59.79
18	80	80	4	77.21	77.46	70.82	70.86
19	60	60	5	69.73	69.80	64.92	65.19
20	60	60	7	53.83	53.51	50.66	51.16

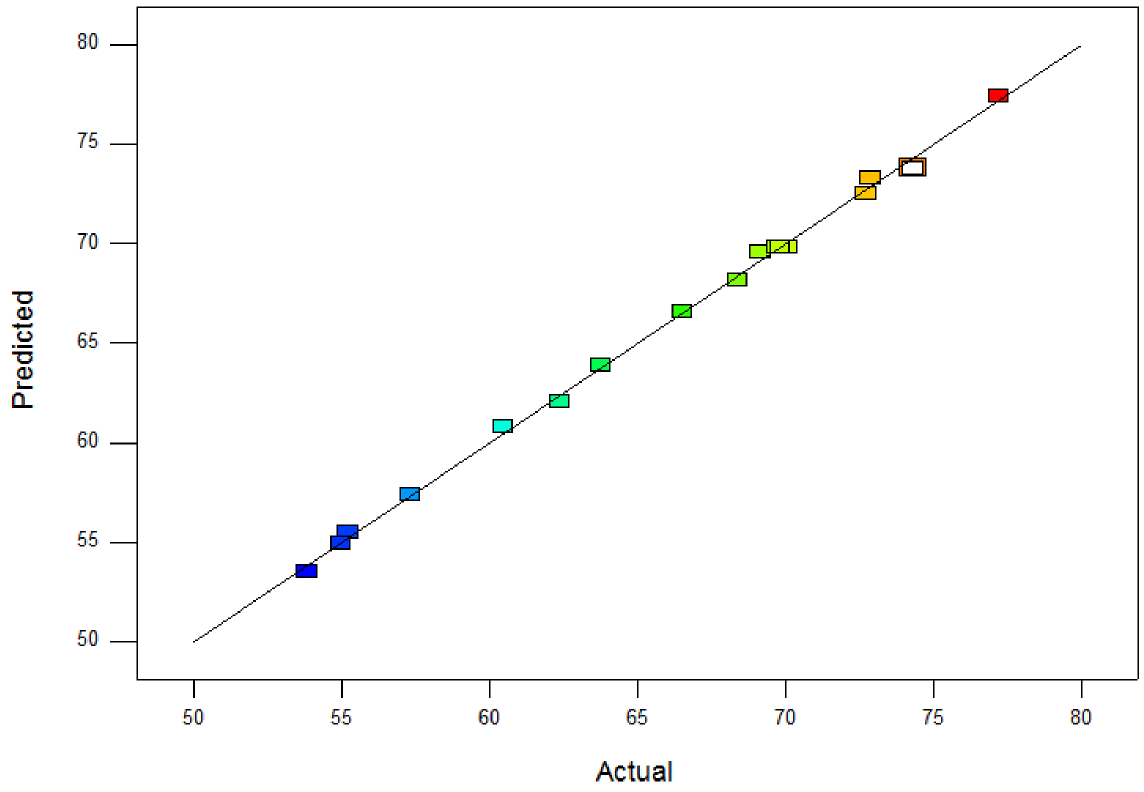


Figure 5.2 Comparison of FAME conversion predicted and actual values

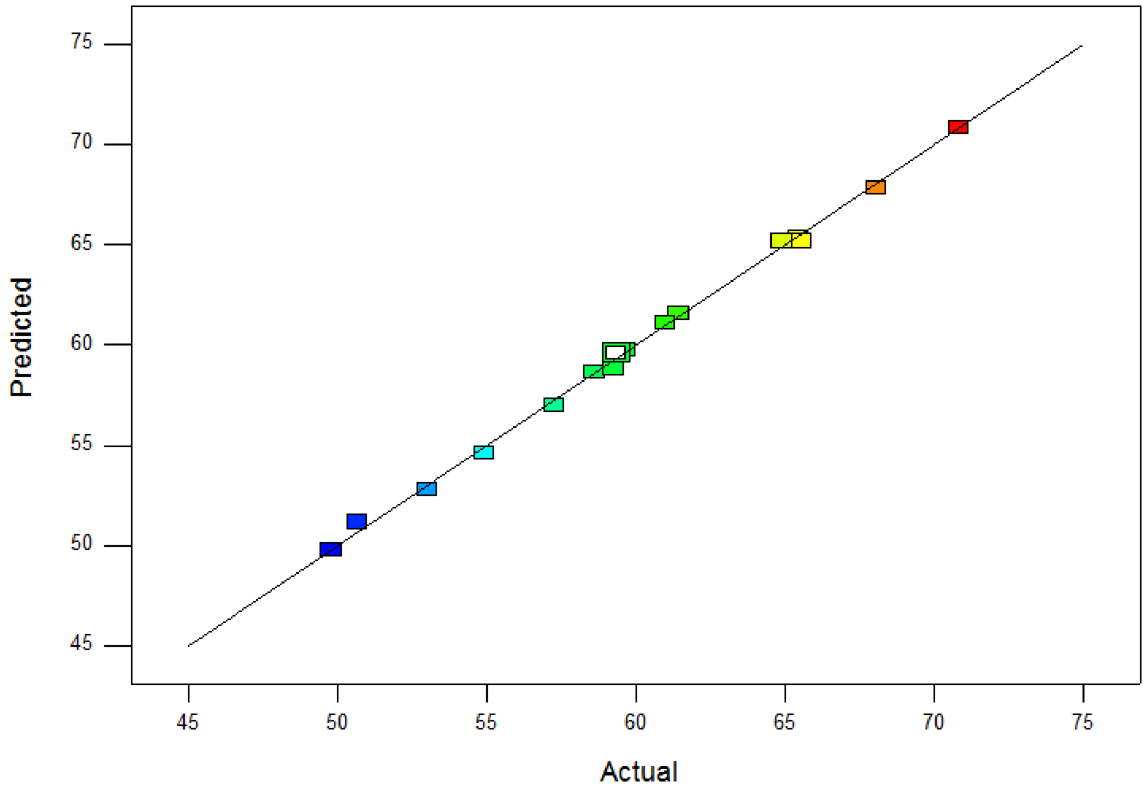


Figure 5.3 Comparison of biodiesel yield predicted and actual values

Table 5.5 Adequacy of models tested for FAME conversion

Source	**Sequential p-value**	**Standard deviation**	**R-squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**Remarks**
Linear	< 0.0001	3.02	0.8380	0.8076	0.7604	
2FI	0.2978	2.92	0.8767	0.8198	0.7724	
Quadratic	< 0.0001	0.36	0.9985	0.9972	0.9888	Suggested
Cubic	0.8272	0.42	0.9988	0.9962	0.7725	Aliased

Table 5.6 Adequacy of models tested for biodiesel yield

Source	**Sequential p-value**	**Standard deviation**	**R-squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**Remarks**
Linear	0.0019	3.99	0.5963	0.5206	0.3601	
2FI	0.3518	3.92	0.6833	0.5371	0.4550	
Quadratic	< 0.0001	0.35	0.9980	0.9963	0.9877	Suggested
Cubic	0.3098	0.32	0.9990	0.9969	0.9155	Aliased

The suitability of models is tested for both FAME conversion and biodiesel yield and are shown in Tables 5.5 and 5.6 respectively. The highest order polynomial should be selected, where the additional terms are significant and model is not aliased. The sequential model sum of squares p-value was high for cubic model and 2 factor interaction model which makes them insignificant. Also the cubic model and higher models are aliased. The sequential p-value was low for linear model and quadratic model. In addition the model which gives maximum "Adjusted R-squared and Predicted R-squared" should be selected. Linear model gives low Adjusted R-squared and Predicted R-squared for both the responses which makes it insignificant. For both the responses FAME conversion and biodiesel yield, quadratic model gives very high Adjusted R-squared and Predicted R-squared which makes the model significant.

5.3.1 Fitting of second order polynomial equation and statistical analysis

Based on the results obtained, the response surface methodology using CCD (Central Composite Design) suggests quadratic model which includes second order terms. Cubic and higher models were aliased whereas linear and 2 factor interaction models were not significant as R-squared values were low.

Analysis of variance (ANOVA) is a statistical technique that divides the total variation in a set of data parts and used for testing the possibilities of variation of the data parts related with particular parameters. The implication of the ratio of mean square variation due to regression and mean square residual error was analyzed using ANOVA. The ANOVA for FAME conversion quadratic model and biodiesel yield quadratic model are presented in Table 5.7 and Table 5.8 respectively.

The ANOVA for FAME conversion implies that the relationship between FAME conversion and operating parameters was well represented by quadratic model. Based on the ANOVA results, the F-value for model is 754, which was very high and implies that model was significant. The p-value of model represents there was only 0.01 % chance that an F-value this large could occur due to noise. Model terms having p-value less than 0.05 are significant. All the model terms (A, B, C, AB, AC, A^2, B^2 and C^2) except BC were highly significant in determining FAME conversion as p-values corresponding to them were very low (<0.0001). Model terms having p-value greater than 0.1 are insignificant. None of the model terms was insignificant. Significance of model term BC was low as p-value corresponding to it was 0.0242. If the difference between Predicted R-squared and Adjusted R-squared is less than 0.2, then the model is suitable. The Predicted R-squared value of 0.9888 was in reasonable agreement with the Adjusted R-squared of 0.9972.

The ANOVA for biodiesel yield implies that the relationship between biodiesel yield and operating variables was well represented by second order model. According to the ANOVA table the F-value for model was 562.66 which was very high implying that model was significant. The p-value of model represents there is only 0.01 % chance that an F-value this large could occur due to noise. All the model terms (B, C, AB, BC, A^2, B^2 and C^2) except A and AC were highly significant in determining biodiesel yield as p-values corresponding to them were very low. None of the model terms are insignificant. Significance of amplitude (A) was moderate and the significance of the product of amplitude and total flowrate (AC) was low. The high value of Predicted R-squared of 0.8211 was in good agreement with the Adjusted R-squared value of 0.9651.

Table 5.7 ANOVA for FAME conversion quadratic model

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p -value Prob > F**	**Remarks**
Model	899.00	9	99.89	754.00	< 0.0001	Highly significant
A-Amplitude	37.18	1	37.18	280.64	< 0.0001	Highly significant
B-Pulse ratio	356.55	1	356.55	2691.36	< 0.0001	Highly significant
C-Total flowrate	360.72	1	360.72	2722.81	< 0.0001	Highly significant
AB	23.36	1	23.36	176.32	< 0.0001	Highly significant
AC	10.60	1	10.60	80.04	< 0.0001	Highly significant
BC	0.93	1	0.93	7.03	0.0242	Significant
A^2	34.72	1	34.72	262.08	< 0.0001	Highly significant
B^2	46.34	1	46.34	349.80	< 0.0001	Highly significant
C^2	72.67	1	72.67	548.56	< 0.0001	Highly significant
Residual	1.32	10	0.13			
Lack of Fit	1.25	5	0.25			
Pure Error	0.070	5	0.014			
Cor Total	900.32	19				

FAME conversion in terms of coded factors:

$$\text{FAME conversion (\%)} = 69.805 + 1.524 * A + 4.721 * B - 4.748 * C + 1.709 * AB + 1.151 * AC - 0.341 * BC - 1.175 * A^2 - 1.358 * B^2 - 1.700 * C^2 \quad \textbf{(5.1)}$$

FAME conversion in terms of actual factors:

FAME conversion (%) = 37.04176 - 0.11537 * Amplitude + 0.47232 * Pulse ratio + 9.82301 * Total flowrate + 0.00427 * Amplitude * Pulse ratio + 0.057563 * Amplitude * Total flowrate - 0.017062 * Pulse ratio * Total flowrate - 0.0029377 * Amplitude^2 - 0.003394 * Pulse ratio^2 - 1.70011 * Total flowrate^2 **(5.2)**

Table 5.8 ANOVA for Biodiesel yield quadratic model

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p -value Prob > F**	**Remarks**
Model	628.98	9	69.89	562.66	< 0.0001	Highly significant
A-Amplitude	1.77	1	1.77	14.25	0.0036	Significant
B-Pulse ratio	96.25	1	96.25	774.92	< 0.0001	Highly significant
C-Total flowrate	277.78	1	277.78	2236.39	< 0.0001	Highly significant
AB	35.11	1	35.11	282.64	< 0.0001	Highly significant
AC	0.77	1	0.77	6.21	0.0319	Significant
BC	18.95	1	18.95	152.59	< 0.0001	Highly significant
A^2	35.15	1	35.15	282.97	< 0.0001	Highly significant
B^2	172.86	1	172.86	1391.72	< 0.0001	Highly significant
C^2	50.87	1	50.87	409.56	< 0.0001	Highly significant
Residual	1.24	10	0.12			
Lack of Fit	0.88	5	0.18			
Pure Error	0.36	5	0.072			
Cor Total	630.22	19				

Biodiesel yield in terms of coded factors:

$$\text{Biodiesel yield (\%)} = 65.186 + 0.333 * A + 2.453 * B - 4.167 * C + 2.095 * AB - 0.310 * AC - 1.539 * BC - 1.182 * A^2 - 2.622 * B^2 - 1.422 * C^2 \quad \textbf{(5.3)}$$

Biodiesel yield in terms of actual factors:

$$\text{Biodiesel yield (\%)} = - 1.02808 + 0.13473 * \text{Amplitude} + 0.97983 * \text{Pulse ratio} + 15.60649 * \text{Total flowrate} + 0.005237 * \text{Amplitude} * \text{Pulse ratio} - 0.015525 * \text{Amplitude} * \text{Total flowrate} - 0.076960 * \text{Pulse ratio} * \text{Total flowrate} - 0.002955 * \text{Amplitude}^2 - 0.006555 * \text{Pulse ratio}^2 - 1.42240 * \text{Total flowrate}^2 \quad \textbf{(5.4)}$$

5.3.2 Effect of process variables

Both FAME conversion and biodiesel yield were dependent on individual process variables and also depend on combined effect of process variables. Effect of individual process variables on both FAME conversion and biodiesel yield are shown in Figure 5.4 and Figure 5.5 respectively.

Amplitude: At centre points of pulse ratio and total flowrate, with an increase in amplitude from the reference point, the increase in FAME conversion is small, and with a decrease in amplitude from the reference point FAME conversion decreases continuously. The change in biodiesel yield is very small with an increase in amplitude from reference point. Biodiesel yield slightly decreases with a decrease in amplitude from the reference point. The effect of amplitude on FAME conversion is severe than on biodiesel yield.

Pulse ratio: At centre points of amplitude and total flowrate, with an increase in pulse ratio from the reference point, the FAME conversion increases progressively, and with a decrease in pulse ratio from the reference point FAME conversion decreases continuously. Biodiesel yield slightly increases with an increase in pulse ratio from the reference point initially, reaches maximum and decreases thereafter. Biodiesel yield decreases continuously with a decrease in pulse ratio from the reference point. The effect of pulse ratio on FAME conversion is severe when compared to biodiesel yield.

Total flow rate: At centre points of amplitude and pulse ratio, with an increase in total flowrate from the reference point, the FAME conversion decreases continuously, and with a decrease in total flowrate from the reference point FAME conversion increases progressively. In a similar way, biodiesel yield decreases progressively with an increase in total flowrate from reference point. Biodiesel yield increases continuously with a decrease in total flow rate from the reference point. The effect of total flowrate on FAME conversion and biodiesel yield occurs to same extent.

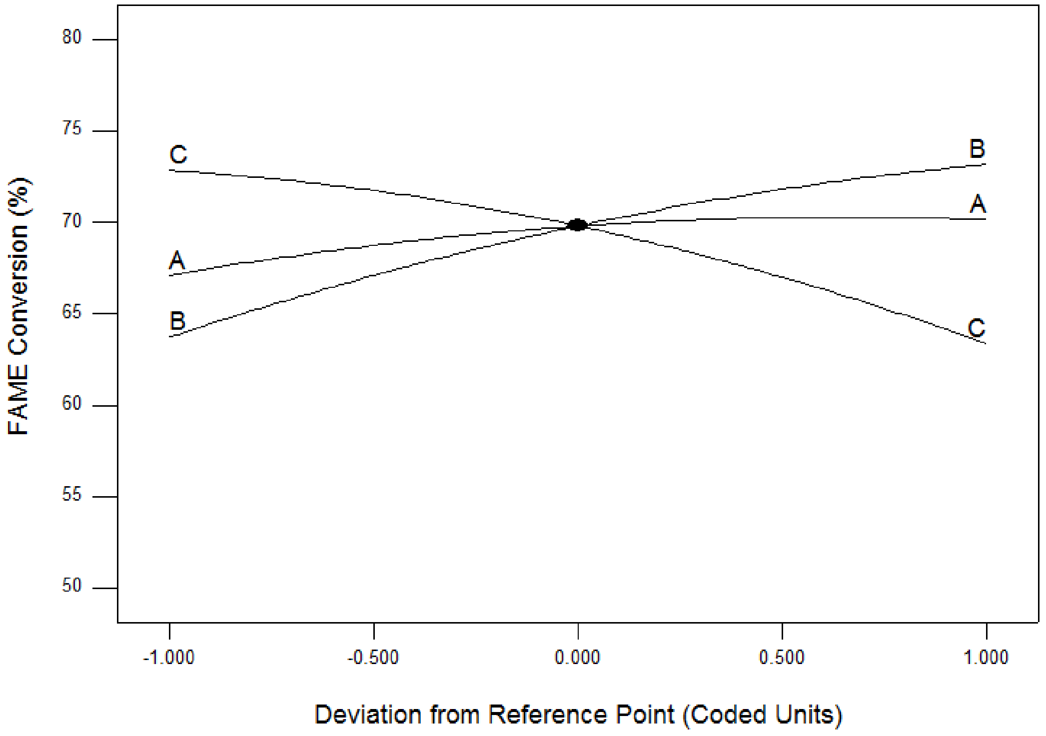


Figure 5.4 Variation of FAME conversion with deviation in process variables

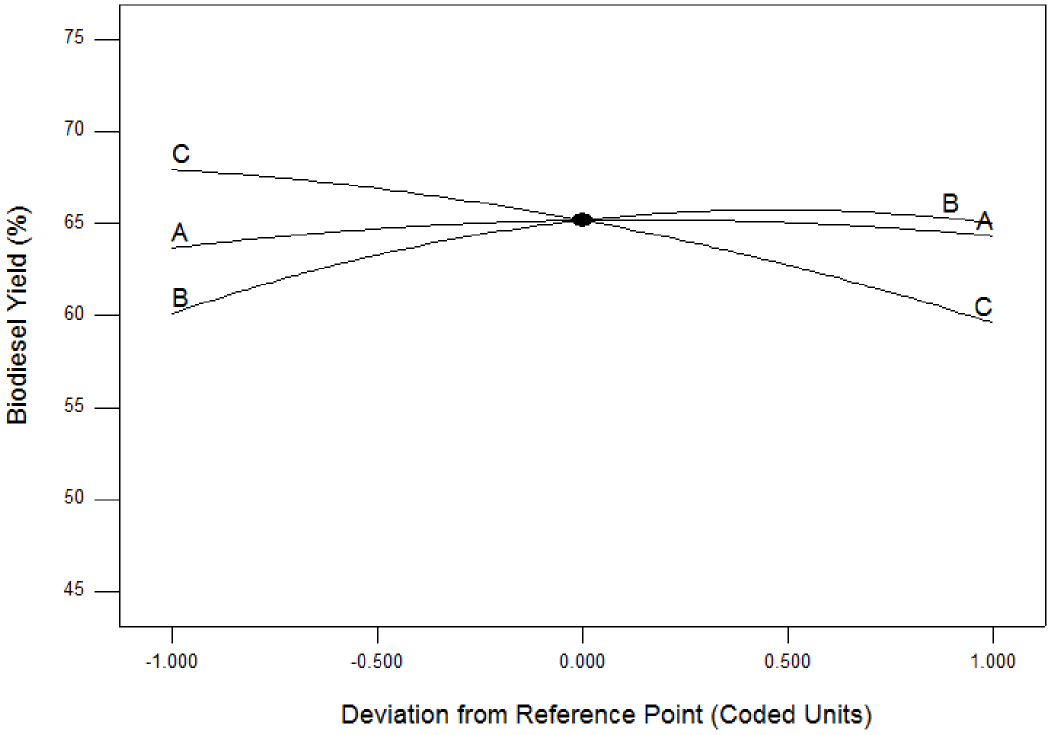


Figure 5.6 Variation of biodiesel yield with deviation in process variables

Effect of pulse ratio and amplitude: The combined effect of pulse ratio and amplitude on FAME conversion and biodiesel yield are shown in Figures 5.6 and 5.7 respectively. At centre point of flowrate, when the pulse ratio is low and amplitude is high, the FAME conversion was minimum and when both pulse ratio and amplitude were high, the FAME conversion was maximum. With an increase in amplitude and pulse ratio simultaneously the FAME conversion increases continuously. The change in FAME conversion with an increase in pulse ratio at constant amplitude was higher at higher amplitude. Similarly, the change in FAME conversion with an increase in amplitude at constant pulse ratio was higher at higher pulse ratio. FAME conversion at low amplitude and high pulse ratio was more than FAME conversion at high amplitude and low pulse ratio. This implies that FAME conversion was highly dependent on the combined effect of pulse ratio and amplitude. Similar kind of effect was observed in the case of biodiesel yield.

Effect of amplitude and total flow rate: The combined effect of amplitude and total flowrate on FAME conversion and biodiesel yield are shown in Figures 5.8 and 5.9 respectively. At centre point of pulse ratio, maximum FAME conversion was attained at low flowrate and high amplitude, minimum FAME conversion was attained at high flowrate and low amplitude. FAME conversion was increased with decrease in flowrate and with an increase in amplitude. The change in FAME conversion with decrease in flowrate at constant amplitude was higher at low amplitude. The change in FAME conversion with increase in amplitude at constant total flowrate was higher at high flowrate. This indicates FAME conversion is highly dependent on combined effect of flowrate and amplitude. With simultaneous increase in amplitude and total flowrate there was gradual decrease in FAME conversion. This implies that total flowrate has a severe effect on FAME conversion. Maximum biodiesel yield was attained at low flowrate and high amplitude. Biodiesel yield is close to minimum at high flowrate for all amplitudes. This implies that the combined effect of `amplitude and total flowrate on biodiesel yield. The change in biodiesel yield with flowrate at constant amplitude is similar for all amplitudes. The change in biodiesel yield with amplitude at constant flowrate is small for all flowrates. This indicates that the combined effect of amplitude and flowrate on biodiesel yield is moderate.

Effect of pulse ratio and total flow rate: The combined effect of pulse ratio and total flowrate on FAME conversion and biodiesel yield are shown in Figures 5.10 and 5.11 respectively. At centre point of amplitude, maximum FAME conversion was attained at low flowrate and high pulse ratio, minimum FAME conversion was attained at high flowrate and low pulse ratio. The change in FAME conversion with pulse ratio at constant total flowrate was little high at high flowrate. The change in FAME conversion with total flowrate at constant pulse ratio was slightly high at low pulse ratio. The FAME conversion at high flowrate and low pulse ratio was almost same as FAME conversion at low flowrate and high pulse ratio. This implies that the combined effect of total flowrate and pulse ratio on FAME conversion is moderate. When pulse ratio was high and total flowrate was low, the biodiesel yield was maximum. It was minimum when pulse ratio was low and total flowrate was high. The change in biodiesel yield with total flowrate at constant pulse ratio was high at high pulse ratio. The change in biodiesel yield with pulse ratio at constant total flowrate was high at low flowrate. The biodiesel yield at high pulse ratio and high flowrate was less when compared to yield at low pulse ratio and low flowrate. This indicates that flowrate has severe effect on biodiesel yield.

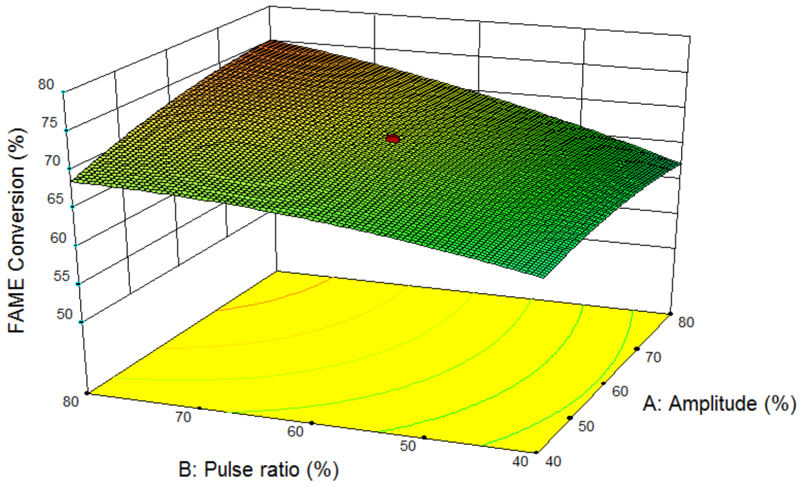


Figure 5.6 Effect of pulse ratio and amplitude on FAME conversion at 5 mL/min total flowrate

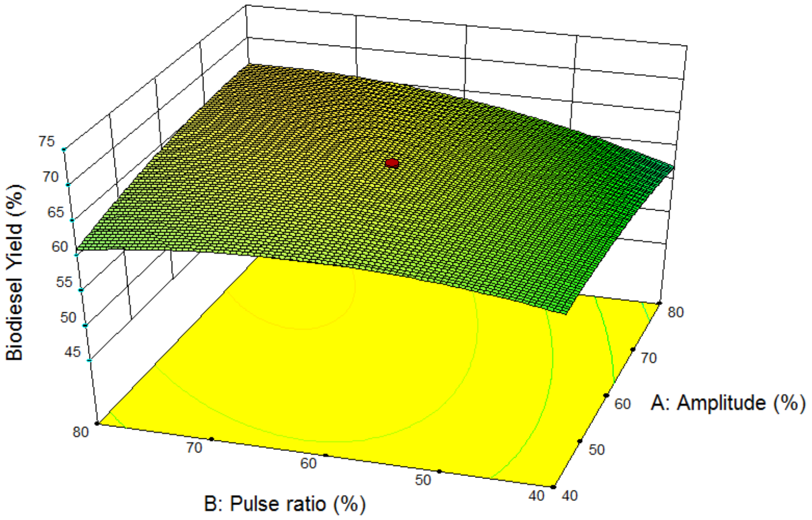


Figure 5.7 Effect of pulse ratio and amplitude on biodiesel yield at 5 mL/min total flowrate

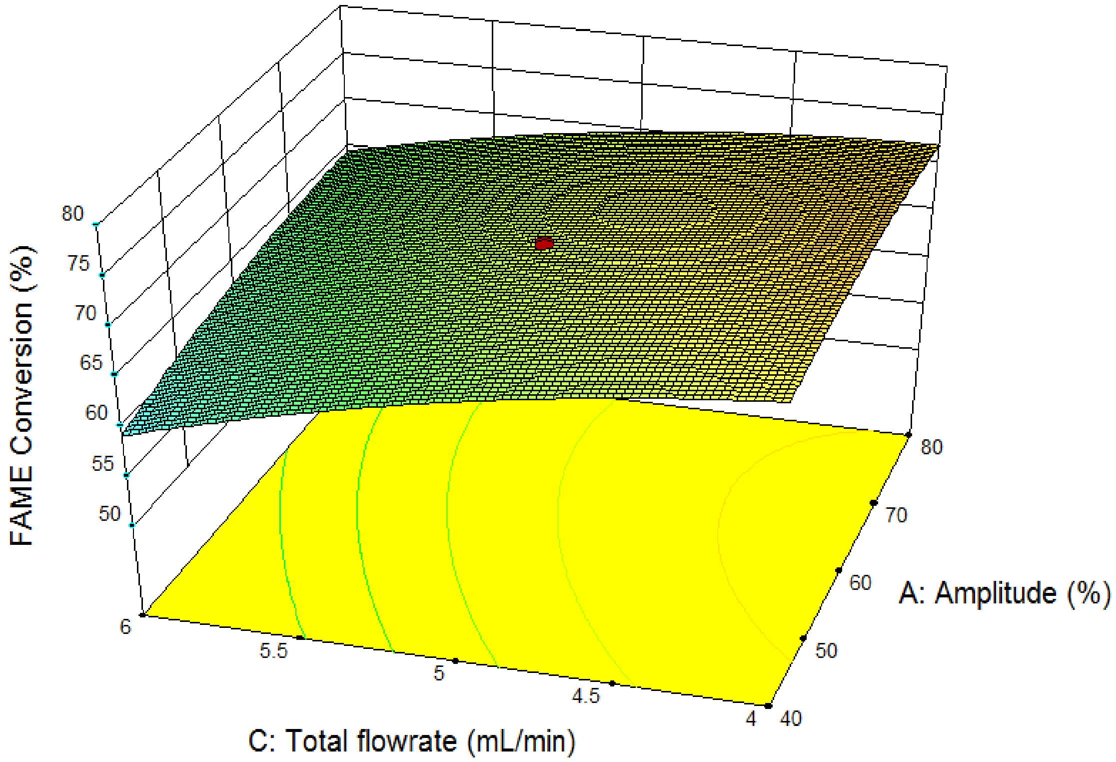


Figure 5.8 Effect of total flowrate and amplitude on FAME conversion at 60 % pulse ratio

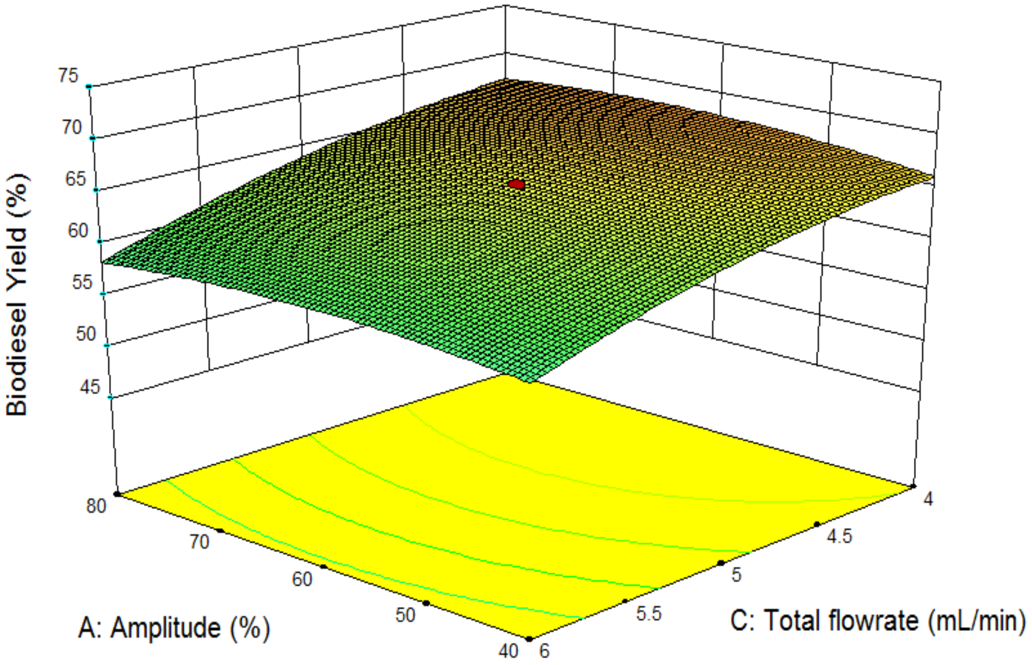


Figure 5.9 Effect of total flowrate and amplitude on biodiesel yield at 60 % pulse ratio

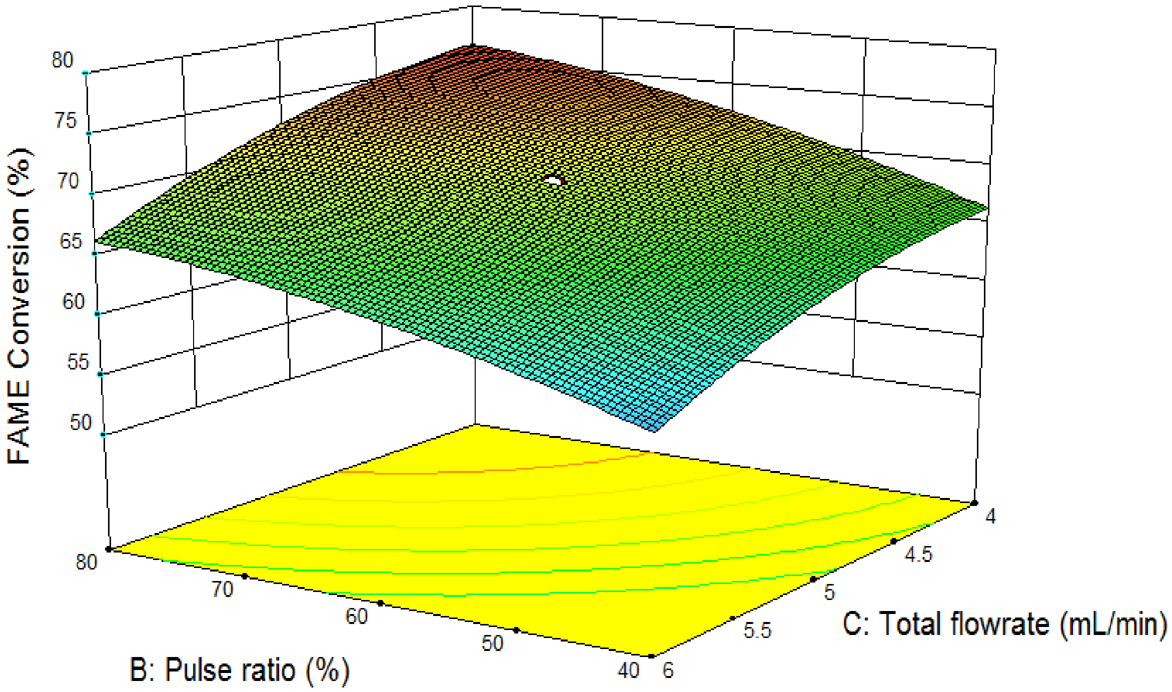


Figure 5.10 Effect of total flowrate and pulse ratio on FAME conversion at 60 % amplitude

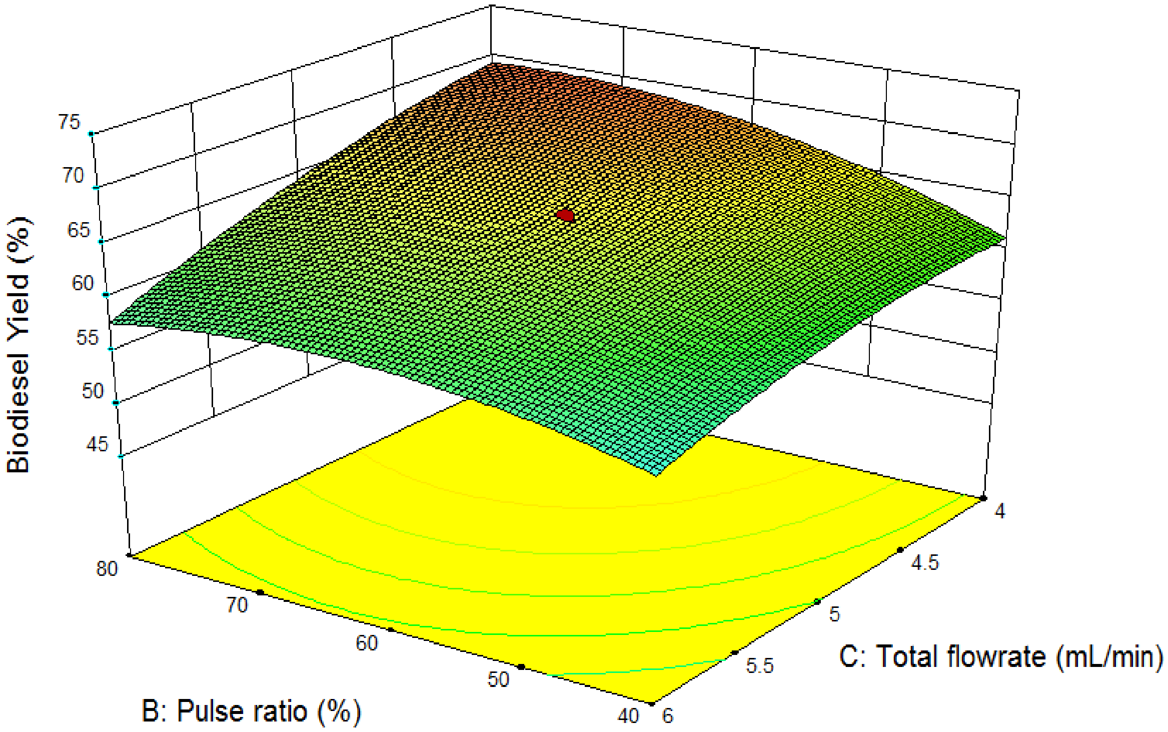


Figure 5.11 Effect of total flowrate and pulse ratio on biodiesel yield at 60 % amplitude

The effect of flowrate and pulse ratio is severe and the effect of amplitude is moderate on FAME conversion. The effect of flowrate is severe, effect of pulse ratio is moderate and effect of amplitude is low on biodiesel yield.

5.3.3 Physical interpretation of the results

The ultrasonic energy propagates through the reaction medium in the form of longitudinal waves with a series of compressions and rarefactions and causes high speed oscillatory motion of fluid elements called micro-streaming. This motion gives rise to intense micro-mixing in the medium that is capable of producing finer emulsion than mechanical stirring resulting in conversion of triglycerides within a short time. The influence of operating parameters was significant on both FAME conversion and biodiesel yield. An increase in amplitude delivers more ultrasonic power to reaction medium which results in high FAME conversion and yield initially. When the amplitude was very high the power supplied was sufficient to break the methyl esters formed which reduces the FAME conversion and biodiesel yield. With an increase in pulse ratio the power supplied to reaction medium was more which results in high FAME conversion and biodiesel yield initially. At very high pulse ratio the amount of biodiesel formed was low. A thick dense material was formed which was a result of emulsification of glycerol with biodiesel and is difficult to separate. As a result, biodiesel yield was observed to be less. With an increase in total flowrate the residence time of fluid inside the reactor decreases which results in low FAME conversion and yield. Conversion and yield can be improved to greater extent by maintaining low flowrates. FAME conversion and biodiesel yield also depends on the ultrasonic irradiation distance. More volume of fluid can be affected by longitudinal vibrations when large irradiation distance is provided. Irradiation distance provided in all experiments may not be sufficient to produce very high FAME conversion and yield.

5.3.4 Optimization and model validation

Statistical optimization of process parameters was carried out to maximize FAME conversion and biodiesel yield. The objective of present work is to produce high amount of biodiesel having uniform quality in a shorter time at lower cost. Figure 5.12 represents the optimum process conditions obtained using quadratic model. Optimized conditions are 64.10% amplitude, 79.88 % pulse ratio and 3.54 mL/min total flowrate. Using quadratic model FAME conversion and biodiesel yield were predicted to be 77.2263 % and 70.8601 % respectively at optimized process conditions. A value of 1 for desirability represents that the FAME conversion and biodiesel yield predicted are greater than highest values obtained in the designed experiments. Validation of model was done by carrying out experiment at optimized process conditions and the results were reported in Table 5.9. The experimental values of FAME conversion and biodiesel yield were close to predicted values.

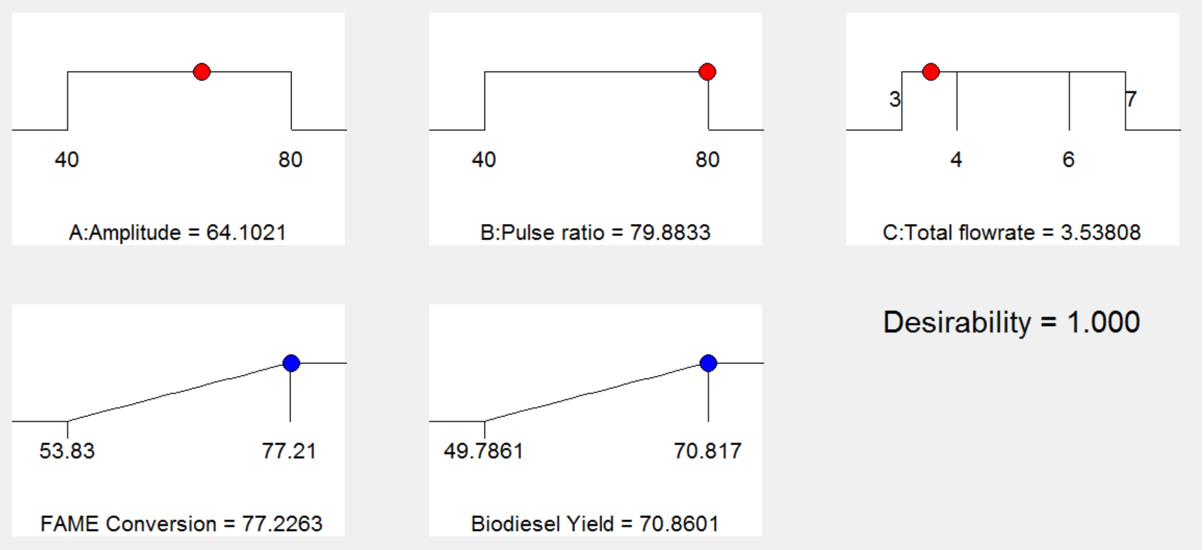


Figure 5.12 Optimization of FAME conversion and biodiesel yield

Table 5.9 Model validation

Operating conditions	**Response**	**Optimal value (predicted)**	**Optimal value (experimental)**
Amplitude- 64 % Pulse ratio- 80 % Total flowrate- 3.5 mL/min	FAME conversion	77.23	76.85
	Biodiesel yield	70.86	70.25

Table 5.10 Physical and chemical properties of biodiesel from continuous process at optimized process conditions

Fuel property	**Standard biodiesel (EN 14214)**	**Biodiesel from continuous process**
Density @ 15.5 ^{0}C, kg/m^3	860 – 900	873.64
Specific gravity @ 15.5 ^{0}C	0.860 - 0.9	0.874
Kinematic viscosity @ 40 ^{0}C, mm^2/s	3.5 - 5.0	4.8
Flash point , ^{0}C	> 101	142
Cloud point, ^{0}C	Location dependent	1
Pour point, ^{0}C	Location dependent	-2

5.4 Energy Consumption in Biodiesel Production

The amount of total energy consumed in the production of biodiesel from both the oils was calculated for batch mixing and batch ultrasonication. The calculations are shown in Annexure-II. The energy consumed for production of one gram of biodiesel is shown in Figure 5.13. Energy consumed using soyabean oil was less when compared to jatropha oil. This was due to the fact that jatropha oil contains high FFA which needs to be pretreated. Pretreatment involves equal amount of energy as batch mixing. Using soyabean oil, the amount of energy consumed in ultrasonication process was very less as compared to batch mixing which makes it energy efficient. Using jatropha oil, the amount of energy consumed in ultrasonication process was approximately half compared to batch mixing. The major amount of energy consumed in ultrasonication process was due to pretreatment of oil.

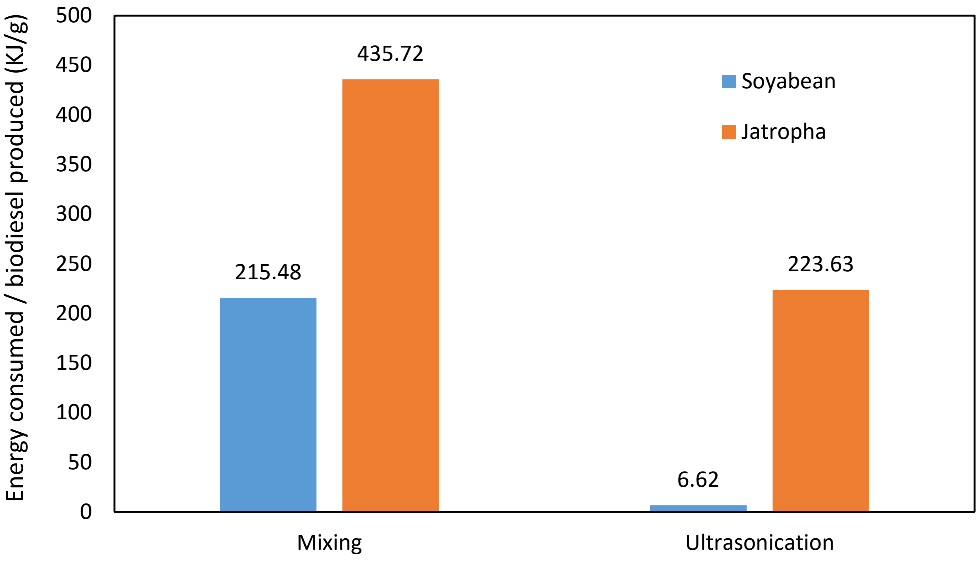


Figure 5.13 Energy consumed per gram of biodiesel produced using various processes

5.5 Comparison of Results from Different Processes

FAME conversion and volume yield using jatropha oil were compared for all the processes. The conversion was noticed to be high using batch ultrasonication followed by batch mixing while the volume yield was high using mixing process. The lowest conversion and yield was observed in the case of continuous process. Ultrasonication intensify the transesterification reaction by impinging the micro jets of one liquid into other. This will result in proper mixing of immiscible reactants and enhance the transesterification reaction. The acoustic effects are severe at higher temperature (50- 60 ^{0}C). Batch ultrasonication was carried out at a temperature nearly equal to 60 ^{0}C which gives 93.83 % conversion. At same temperature, the conversion was 92.02 % using batch mixing. Continuous process was carried out at temperature of 35-40 ^{0}C where the cavitation effects were moderate due to which the conversion was 77.2 % which was low. Volume yield was high in case of mixing because of better separation of products. Volume yield was low in continuous process. This was because the volume of jatropha processed was low and also some amount of biodiesel got deposited on reactor walls and pipelines, which was difficult to separate. Figures 5.14 and 5.15 shows the FAME conversion and volume yield, respectively, using different processes.

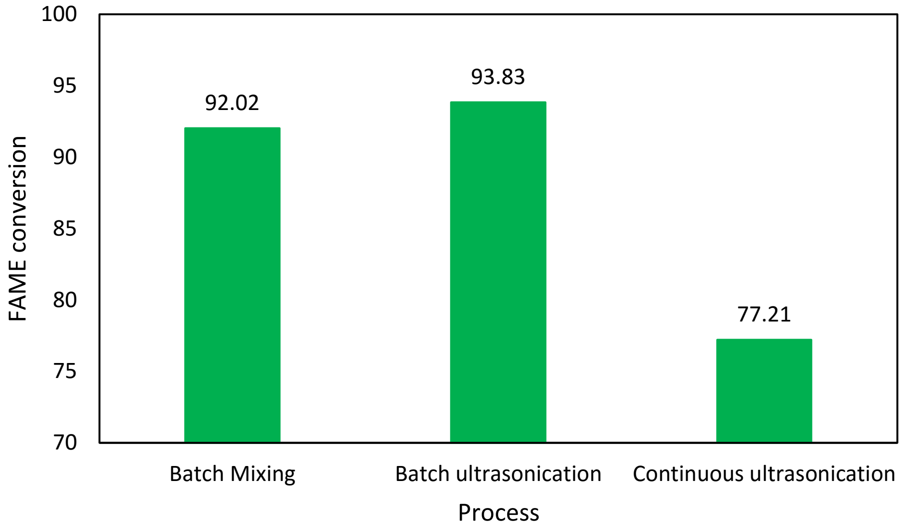


Figure 5.14 FAME conversion using different processes

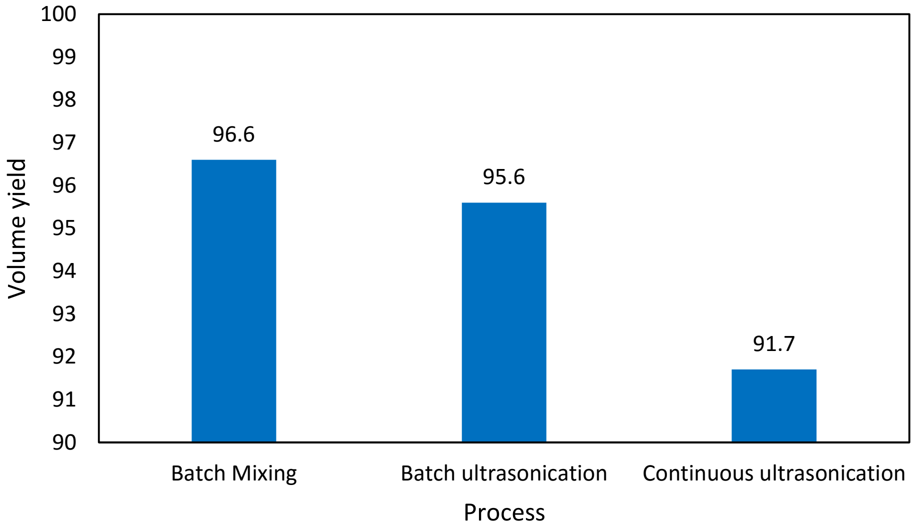


Figure 5.15 Volume yield using different processes

CHAPTER 6

CONCLUSIONS & RECOMMENDATIONS

The need for biodiesel as an alternative for petroleum based diesel is increasing day by day because of various advantages, such as biodegradability, non-toxicity, lower emissions, negligible sulphur content, higher combustion efficiency and superior flash point. But the major disadvantage is its high production cost. There is large scope for biodiesel production in India as number of non-edible plants are native to India. Transesterification of vegetable oils is the common method for biodiesel production which mainly depends upon alcohol: oil molar ratio, type and amount of catalyst and temperature.

In the present work FAME were produced by transesterification of both edible and non-edible oils using methanol in batch process using both stirring and ultrasonication. Biodiesel synthesis from jatropha oil was carried out in a two-step process, first step involves acid catalyzed esterification of jatropha oil with methanol in presence of sulphuric acid to reduce the FFA content in the oil followed by base catalyzed transesterification of esterified jatropha oil with methanol in the presence of sodium methoxide. Biodiesel synthesis from soyabean oil was carried out in a single step process.

This work also focusses on ultrasonic assisted biodiesel production from jatropha oil in continuous process. A new experimental setup was designed for continuous process. Proposed production process involves many steps and are shown in Figure 6.1.

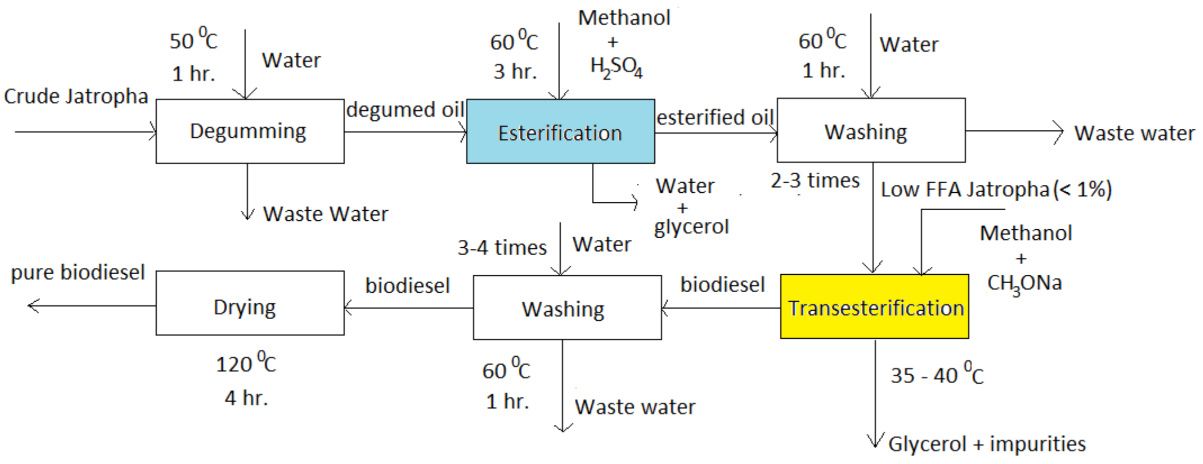


Figure 6.1 Proposed flow diagram of biodiesel production

First step was degumming of jatropha oil with water, after which it was esterified with methanol to reduce FFA content. Third step involves washing of esterified oil with water, which was then transesterified with methanol. Purification step involves separation of formed biodiesel, which was water washed, and dried to produce pure biodiesel. Optimization of process parameters amplitude, pulse ratio and total flow rate was done using RSM. Amplitude and pulse ratio were varied from 20 % to 100 % whereas total flowrate was varied from 3 mL/min to 7 mL/min. 6:1 alcohol to oil molar ratio, 1 wt. % catalyst concentration was taken during all experiments. In total, 20 experiments were designed using CCD method in Design Expert software.

6.1 Conclusions

1. For soyabean and jatropha oils, the FAME conversion using batch ultrasonication is 94.84 % and 93.83 % and is 92.85 % and 92.02 % using batch mixing respectively.
2. For soyabean and jatropha oils, the biodiesel yield using batch ultrasonication is 90.57% and 89.70 % and is 89.32 % and 88.89 % using batch mixing respectively.
3. Using ultrasonic assisted continuous process, the maximum FAME conversion and biodiesel yield obtained were 77.21 % and 70.82 % respectively at 80 % amplitude, 80% pulse ratio and 4 mL/min total flowrate.
4. Parameter optimization was done and optimized conditions were determined to be 64% amplitude, 80 % pulse ratio and 3.5 mL/min total flowrate where FAME conversion and biodiesel yield were found to be 76.85 % and 70.25 % respectively.
5. Energy consumption per gram of biodiesel produced was lowest using ultrasonication process which makes it energy efficient process.

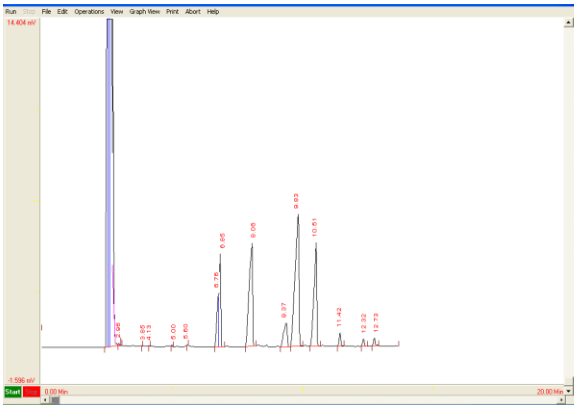
6.2 Recommendations

1. The amount of FAME conversion and biodiesel yield can be improved greatly by decreasing the flowrate thereby providing more residence time for reaction to occur.
2. Operating at high temperatures around 60^0 C may also result in high FAME conversion and biodiesel yield because of intense mixing of the immiscible reactants.
3. Using high amount of base catalyst (1.5 wt. %) can also improve the biodiesel `yield.
4. By increasing the ultrasonic irradiation distance, more amount of active volume was affected by longitudinal vibrations.
5. The ultrasonic assisted continuous process becomes energy efficient if operated at large volumes.

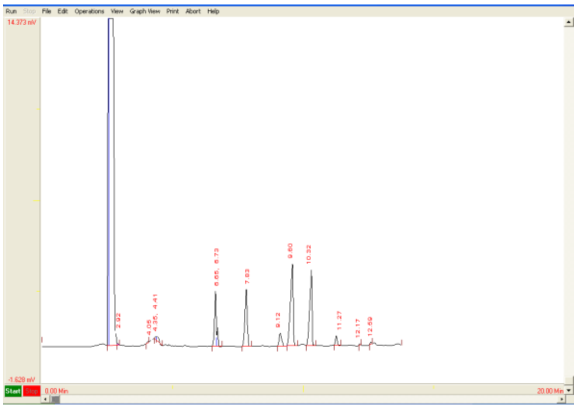
ANNEXURE - I

GC graphs

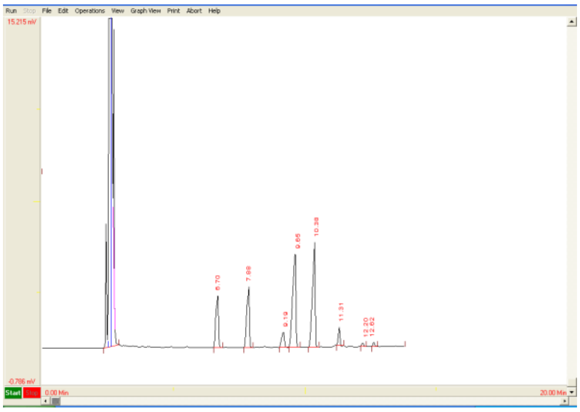
GC graphs for the experiments in continuous process are shown below.



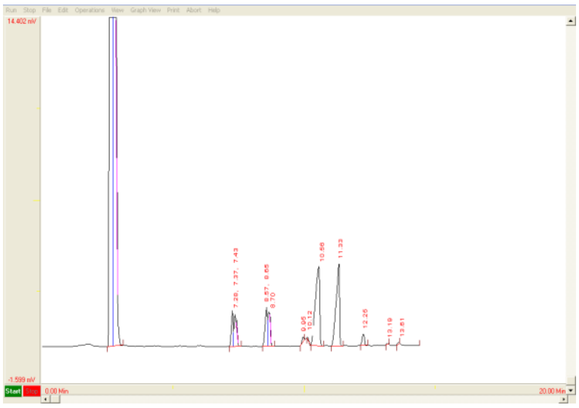
Experiment 1



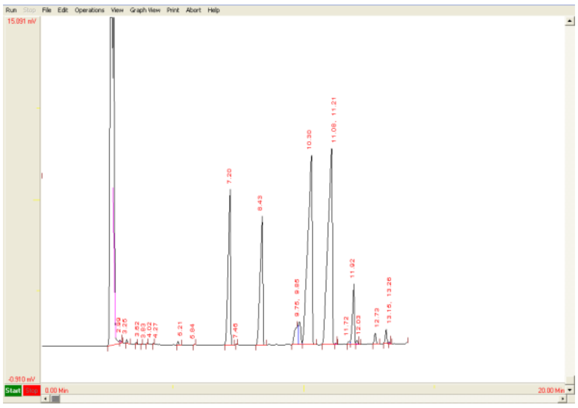
Experiment 2



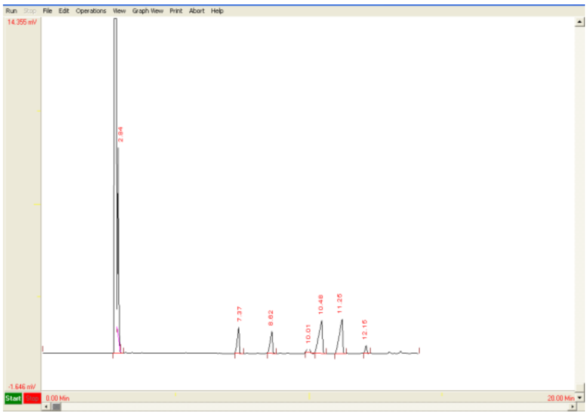
Experiment 3



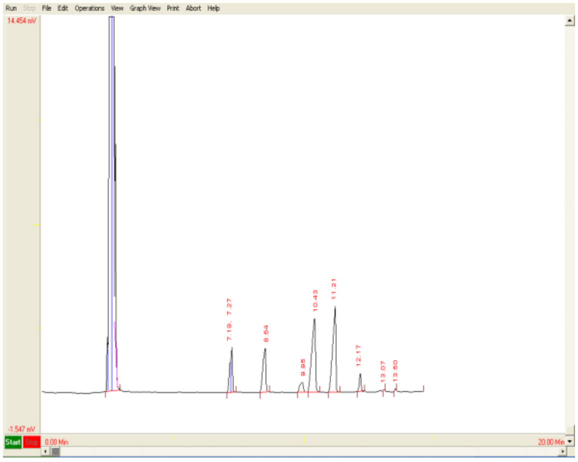
Experiment 4



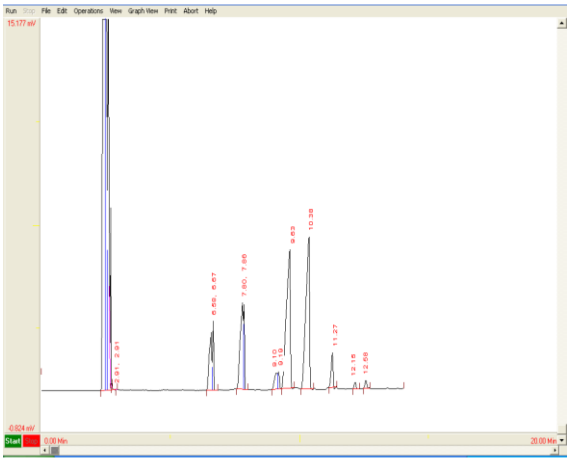
Experiment 5



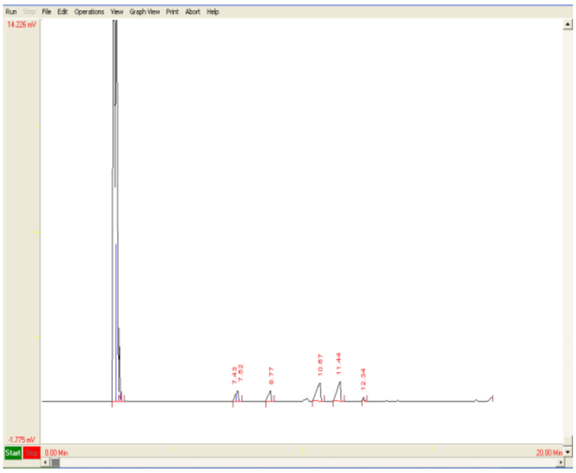
Experiment 6



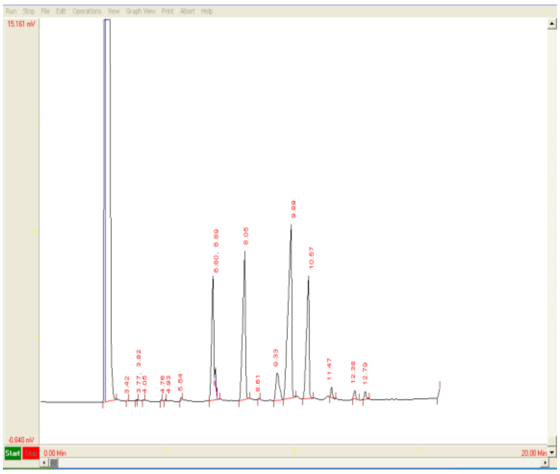
Experiments 7,8, 11, 12, 15, 19



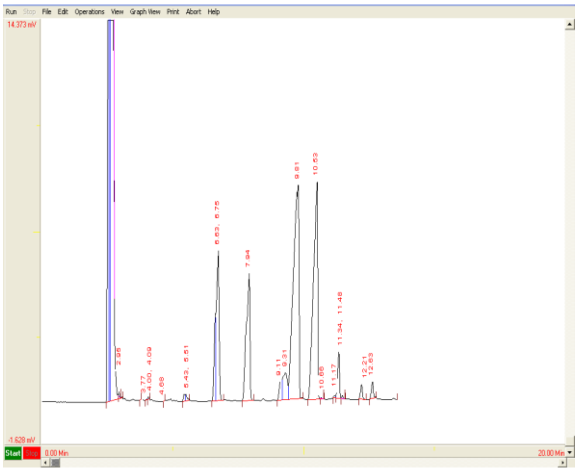
Experiment 9



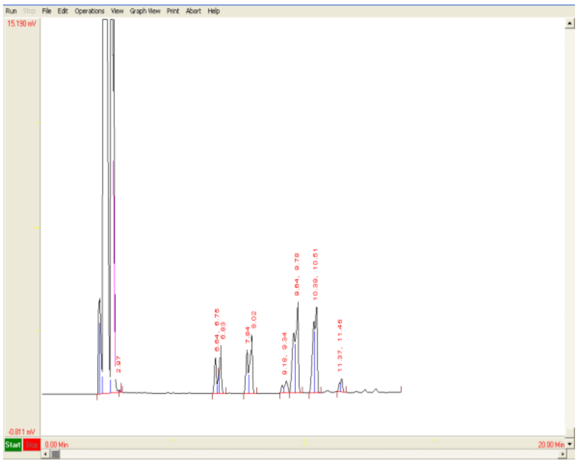
Experiment 10



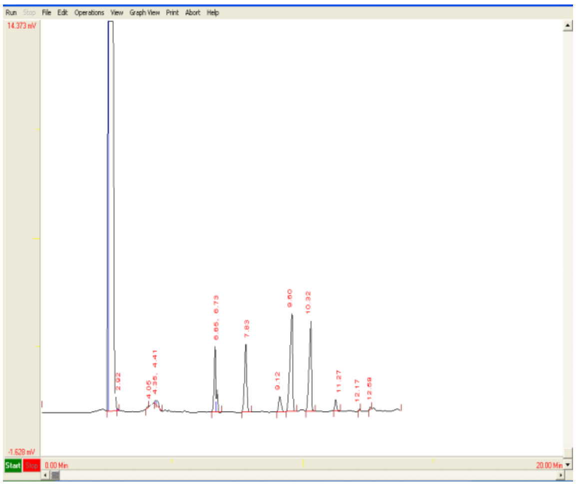
Experiment 13



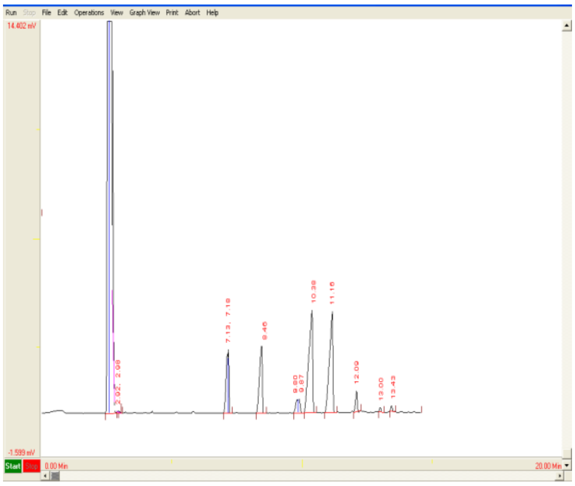
Experiment 14



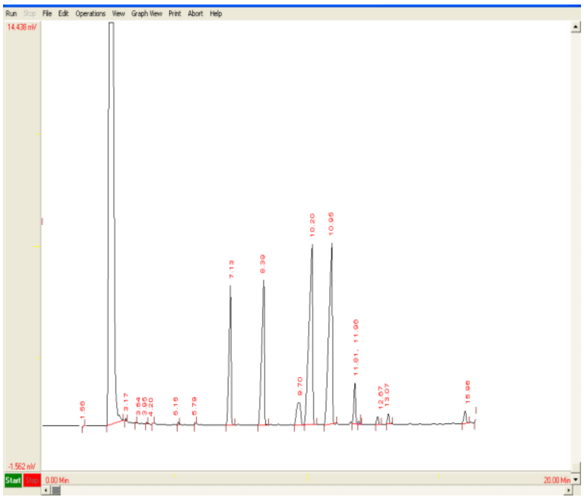
Experiment 16



Experiment 17



Experiment 18



Experiment 20

ANNEXURE - II

Energy consumption calculations

Soyabean oil:

i) Batch mixing:

Power supplied to the magnetic stirrer = voltage × current = 220 × 4.9 =1078 W = 1.078 kW

Operating time = 3 hr.

Energy consumed = 1.078 × 3 = 3.234 kWh = 11642.4 kJ

Amount of oil taken = 0.2 mole

Amount of biodiesel formed = 0.2 × 0.8932 = 0.17864 mole = 0.17864 × 302.45 = 54.03 g

Energy consumed per gram of biodiesel produced = 11642.4/54.03 = 215.48 kJ/g

ii) Batch ultrasonication:

Power supplied to sonicator = 400 W = 0.4 kW

Operating time = 15 min = 0.25 hr.

Energy consumed = 0.4 × 0.25 = 0.1 kWh = 360 kJ

Amount of oil taken = 0.2 mole

Amount of biodiesel formed = 0.2 × 0.9057 = 0.18114 mole = 0.18114 × 300.23 = 54.38 g

Energy consumed per gram of biodiesel produced = 360/54.38 = 6.62 kJ/g

Jatropha:

i) Batch mixing:

Energy consumed in esterification = 3.234 kWh

Energy consumed in transesterification = 3.234 kWh

Energy consumed = 2 × 3.234 kWh = 6.468 kWh = 23284.8 kJ

Amount of oil taken = 0.2 mole

Amount of biodiesel formed = 0.2 × 0.8889 = 0.17778 mole = 0.17778 × 300.62 = 53.44 g

Energy consumed per gram of biodiesel produced = 23284.8/ 53.44 = 435.72 kJ/g

ii) Batch ultrasonication:

Energy consumed = 3.234 + 0.1 = 3.334 kWh = 12002.4 kJ

Amount of biodiesel formed = 0.2 × 0.897 = 0.1794 mole = 0.1794 × 299.15 = 53.67 g

Energy consumed per gram of biodiesel produced = 12002.4 /53.67 = 223.63 kJ/g

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