BIODIESEL PRODUCTION USING CAVITATION TECHNIQUES

A thesis submitted in fulfilment of the requirement for the degree of

Doctor of Philosophy (Ph.D.) in Mechanical Engineering

by

SHASHANK MOHAN (2K14/Ph.D/ME/07)

Under the guidance
of

Prof. AMIT PAL and Prof. RAJ KUMAR SINGH

Department of Mechanical Engineering
DELHI TECHNOLOGICAL UNIVERSITY

ACKNOWLEDGEMENTS

I express my deep gratitude to my supervisors Prof. Amit Pal and Prof. Raj Kumar Singh for assisting me in identifying and formulating the research problem. Their valuable guidance and support has been of great use for me in conducting experiments and completing this research work.

I also express my special thanks to Prof. R.S. Mishra, Head of Mechanical Engineering Department, DTU for his continued inspiration and support during this research work.

I would like to thank all the faculty members, lab assistants and technicians of Mechanical Engineering Department, DTU for their support whenever required, resulting in successful completion of my Ph.D. research work. I would like to thank to all those who directly and indirectly supported me in carrying out this thesis work successfully.

Furthermore, I would like to express my deep gratitude to my parents and every member of my family for their endless inspiration, support and guidance throughout my whole life.

(Shashank Mohan)

2K14/PhD/ME/07

ABSTRACT

The increasing industrialization and motorization of the world has lead to steep rise in the demand of petroleum based fuels. Moreover the finite reserves of crude oil are concentrated in certain regions of the world and most of the developing countries are net importer of the crude oil. Large outflow of foreign exchange and uncertainty in its availability is a matter of major concern for the developing countries like India. Excessive use of fossil fuels also resulted in global environmental degradation effects such as smog, greenhouse effect, acid rain, ozone layer depletion, climate change, etc. The main reason for increased pollution level inspite of stringent emission norms that have been enforced, is the increased demand for energy in all sectors and most significantly in the transport sector. Depleting reserves of crude petroleum, uncertainty in availability, environmental degradation and the rapid hike in petroleum prices have lead to search for the alternate fuels, with particular emphasis on the biofuels, that possess the advantage of being renewable and showing an ad-hoc advantage in reducing CO_2 emissions. Biofuels made from agricultural products (oxygenated by nature) reduce the dependence on oil imports, support local agricultural industries and enhances farming incomes. Moreover, they also benefit in terms of reduced smokiness or particulate matter in engine exhausts. There are several factors that need to be taken care before recommending any alternate fuel to be used with existing technologies on a large scale. The main factors are stated below:-

- ✓ Extent of modification required in existing hardwares, i.e., if any alternate fuel needs extensive modification in the existing hardware involving huge capital investment, then it may be difficult to implement.

- ✓ The investment cost for developing infrastructure to manufacture and supply of these alternate fuels. The excessive infrastructure cost may act as a deterrent to the development of the alternate energy resources.
- ✓ Environmental compatibility as compared to conventional fuels.
- ✓ Additional cost to the user in terms of routine maintenance, equipment wear and lubricating oil life. The excessive additional cost will have an adverse effect on the widespread acceptance of alternate fuels.

Biodiesel is an alternate fuel, which has a high potential to gradually replace petro-diesel as it satisfies most of the parameters mentioned above.

This research work primarily focus on conversion of non-edible oils into their methylesters. Oil extracted from Jatropha seeds forms the background of the experiments, however new oils such as Deodar oil and Semal oil were also explored and investigated for the first time.

The present work highlights the advantages of using cavitation techniques for biodiesel production. A framework for optimization of various process parameters such as Molar ratio, Catalyst concenteration, Reaction time and Power supplied to ultrasonic transducers has been presented for biodiesel production from various types ultrasonic cavitation reactors. The optimization of these process parameters were also performed on a closed loop ultrasonic reactor. The set up of closed loop ultrasonic reactor was made for large scale batch type biodiesel production. Moreover the biodiesel production was carried out at different pressures. Ultrasonic irradiation in reaction mixture flowing under pressurized conditions resulted in significant reduction in reaction time. The closed loop ultrasonic reactor was then converted into a combined process reactor in order to increase the efficiency and reliability of the system. The set up consist of a closed-loop circuit comprising a feed tank connected with a mechanical stirrer, a reciprocating pump and an ultrasonic reactor. Optimization of process parameters were also carried out for closed loop ultrasonic reactor.

The economic viability of the power required for transesterification of vegetable oil into biodiesel is than carried out in terms of energy efficiency and energy use index. Energy requirements of biodiesel production under optimized conditions are then compared for various ultrasonic reactors for small scale and large scale biodiesel production. Overall energy balance is then carried out for various ultrasonic reactors.

Double and Triple frequency flow cells showed improved reaction yield, reduced reaction time, reduced catalyst requirement and molar ratio, lower Specific Energy consumption and higher Energy Use Index.

Power requirement increases whereas considerable reduction in optimal reaction time was observed in case of ultrasonic irradiation at pressurized condition as compared to ultrasonic irradiation in unpressurised flow of reaction mixture. The latter effect dominates and overall reduction in energy requirement was noticed in case of pressurised ultrasonics. The requirement of molar ratio and catalyst concenteration also reduces under pressurised ultrasonic conditions.

Combined process reactor performed better on most of the parameters as compared to closed loop ultrasonic reactors, however the major advantage was improved reliability of biodiesel production system.

Property testing of biodiesel so produced was carried out and most of the properties of the biodiesel were within the acceptable limits of Bureau of Indian Standards. Oxidative stability of Jatropha oil methyl esters was not lying within acceptable limits. The oxidative stability can be increased by use of suitable antioxidants.

DELHI TECHNOLOGICAL UNIVERSITY

(Govt. of National Capital Territory of Delhi)

BAWANA ROAD, DELHI- 110042

CERTIFICATE

This is to certify that the work embodied in the thesis research proposal entitled **“Biodiesel Production Using Cavitation Techniques”** by **Shashank Mohan, Roll No. 2K14/PhD/ME/07** as a Ph.D. scholar in Department of Mechanical Engineering, Delhi Technological University is satisfactory and meets Ph.D. requirement. This thesis work is useful to utilities based on innovations and research. He has completed his thesis work under our guidance and supervision. The matter embodied in this research work has not been submitted earlier for the award of any degree or diploma to the best of our knowledge and belief.

Prof. Amit Pal	**Prof. Raj Kumar Singh**
(Dept. of Mechanical Engineering)	(Dept. of Mechanical Engineering)
Delhi Technological University	Delhi Technological University

LIST OF ABBREVATIONS

ANN	Artificial Neural Network
ASTM	American Society For Testing Materials
BIS	Bureau of Indian Standards
BS	British Standards
BSFC	Brake Specific Fuel Consumption
BTE	Brake Thermal Energy
CBN	Dichlorobenzene
CCD	Central Composite Design
CI	Compression Ignition
CFPP	Cold Filter Plugging Point
CN	Cetane Number
CP	Cloud Point
CPR	Combined Process Reactor
CSO	Cotton Seed Oil
CSOME	Cotton Seed Oil Methyl Esters
DEE	Diethyl Ether

EGR	Exhaust Gas Recirculation
EN	Norme Europeenne
EUI	Energy Use Index
FFA	Free Fatty Acid
FAME	Fatty Acid Methyl Esters
GHG	Green House Gases
GWP	Global Warming Potential
HC	Hydrodynamic Cavitation
HPA	Heteropoly Acid
HPLC	High Performance Liquid Chromatography
IC	Internal Combustion
IEA	International Energy Agency
ISO	International Organisation for Standardisation
JCO	Jatropha Curcas Oil
LCV	Lower Calorific Value
LCA	Life Cycle Analysis
M:O	Methanol to Oil

MT	Million Tonnes
MS	Mechanical Stirring
NRE	Non Renewable Energy
PP	Pour Point
PU	Power Ultrasonics
PM	Particulate Matter
RBOME	Rice Bran Oil Methyl Ester
RIE	Respiratory Inorganic Effects
RSM	Response Surface Methodology
SEC	Specific Energy Consumption
TAP	Terrestrial Acidification Potential
THC	Total Hydrocarbon
THF	Tetrahydrofuran
TMCS	Trimethylchlorosilane
UR	Ultrasonic Reactor
WCO	Waste Cooking Oil
XRD	X Ray Diffraction

INDEX

S.No. **CONTENTS** **Pages**

CHAPTER 1 INTRODUCTION

CHAPTER 2 LITERATURE REVIEW

CHAPTER 3 RESEARCH METHODOLOGY

CHAPTER 4 OPTIMIZATION OF SMALL SCALE BIODIESEL PRODUCTION THROUGH ULTRASONIC CAVITATION

CHAPTER 5 OPTIMIZATION OF BIODIESEL PRODUCTION THROUGH CLOSED LOOP ULTRASONIC REACTORS

CHAPTER 6 OPTIMIZATION OF BIODIESEL PRODUCTION THROUGH COMBINED PROCESS REACTORS

CHAPTER 7 ECONOMIC ANALYSIS OF BIODIESEL PRODUCTION

CHAPTER 8 CONCLUSIONS AND SCOPE OF FUTURE WORK

REFERENCES

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background

Energy forms the basis of life and foundation of human existence. It is one of our most essential resources without which life would cease. Socio-Economic development of human beings worldwide is measured by the Human Development Index which evaluates per capita energy consumption apart from living standard, life expectancy and literacy rate. The use of energy plays a vital role in development of the human society. Managing the use of energy is inevitable in any functional society. The energy is most important input for growth of all key sectors like agricultural, industrial and transport sectors.

The rapid industrialization and motorization of the world in the past century has led to a sharp increase in the demand of energy. Never decreasing thrust of energy is fulfilled by lavish extraction of non-renewable fossil fuels. Non-renewable sources of energy are on the verge of depletion in near future and cannot be reproduced in a short period of time. Once a non-renewable energy source gets depleted, it will not be replaced within the span of human time scales. Non-renewable energy sources are the underground reserves of hydrocarbons, found in liquid, gas and solid states. Coal, Petroleum and Natural Gas are the major non renewable fossil fuel sources which were formed over millions of years by the action of heat and pressure on dead organic materials. Moreover, crude petroleum has the major share in satisfying the energy requirements of the world (BP Energy Outlook, 2017) as shown in Figure 1.1. The gradual transition in the fuel mix is observed with increasing share of renewables. Renewables together with nuclear and hydroelectric power generation is expected to account for half of the growth in energy supplies over the next 20 years. Even so, oil, gas and coal remain the dominant sources of energy powering the world economy, accounting for more than three-quarters of total energy supplies in 2035 (BP Energy Outlook, 2017).

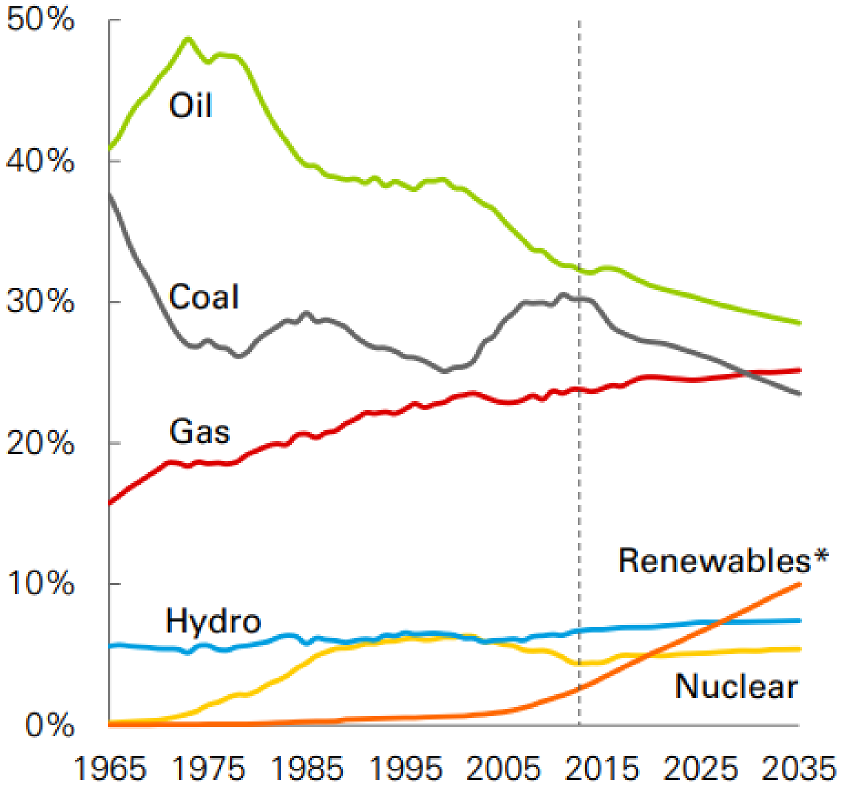


Fig. 1.1: Percentage share of various sources in satisfying energy requirement (BP Energy Outlook, 2017)

Figure 1.2 shows the estimated life of fossil fuel reserves in world as per the current rate of consumption. It is estimated that reserves of oil and gas will deplete much sooner than coal reserves (BP Statistical Review of World Energy, 2016).

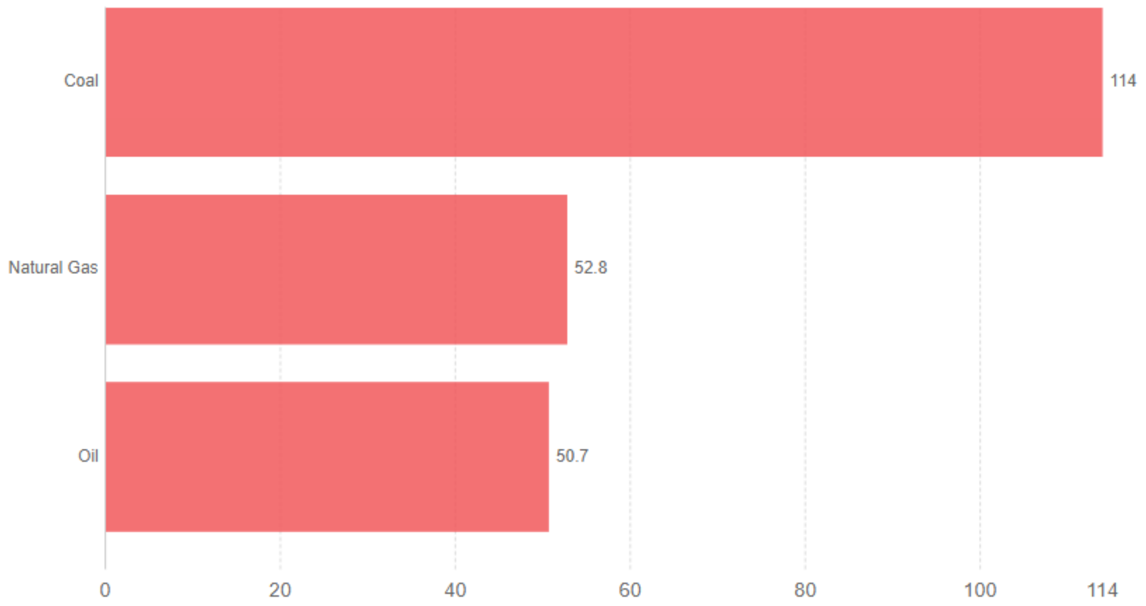


Fig. 1.2: Estimated life of fossil fuels (in years) (BP Statistical Review of World Energy, 2016)

Transportation accounts for around 25% of world energy demand and 61.5% of all the crude oil used every year (Ghazali et al., 2015). It is estimated that the global energy use for transportation purpose is expected to grow at an average rate of 1.8% per year from 2005 to 2035 as per U.S Energy Information Administration, 2010. Figure 1.3 shows projected total world oil consumption between 2007 and 2035.

“Energy security” now a days is very important issue both for developed or developing countries. It has been on the top priority of every government because it can provide the much needed growth for any country. The production and distribution of energy need to be reliable so as to withstand ups and downs associated with its availability and price. The situation worsens as the petroleum reserves are highly concentrated in certain regions of the world (Agarwal, 2007), with India being net importer of crude oil. India is projected to become the third largest consumer of transport fuel by 2020, after USA and China, with consumption growing at an annual rate of 6.8%. (Pal et al., 2010). The huge outflow of foreign exchange on one hand and the increase in the price of crude oil on the other hand have affected the development of India. However, whilst depleting reserves could become a pressing issue 50-100 years from now, there is another important limit to fossil fuel production: climate change. The indiscriminate utilization of fossil fuels has resulted in environmental degradation due to global warming, acid rain, smog, deforestation, shift in climatic conditions and serious modifications in earth's surface. Fossil fuels are the key contributor of carbon dioxide (CO2), nitrogen oxide (NOx), hydrocarbons (HC) and PM emissions.

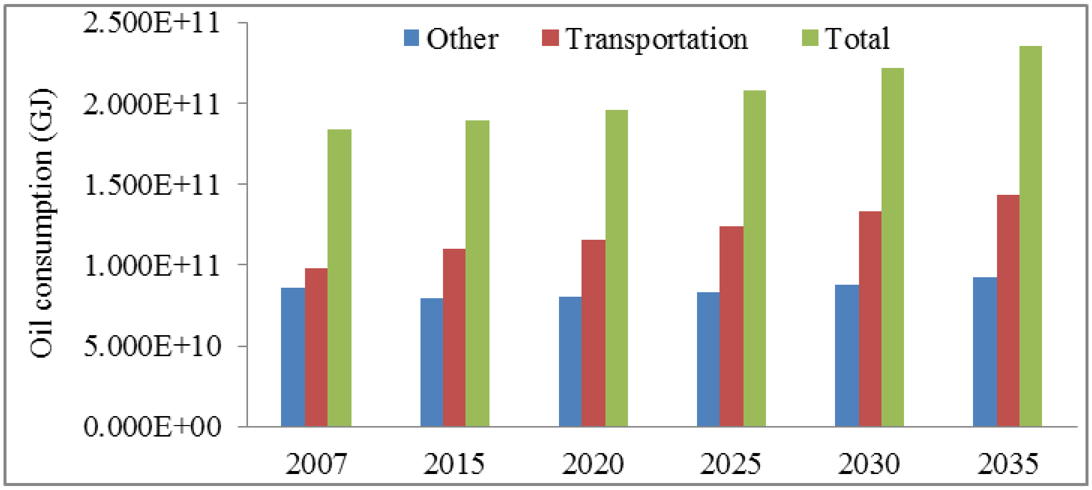


Fig. 1.3: Total world oil consumption between 2007 and 2035 (U.S Energy Information Administration, 2010)

The depleting oil reserves, escalating prices, uncertainty in its availability and environmental degradation are the important factors initiating the search for an alternative and cleaner source of energy, which can supplement or replace petrodiesel (Pal, Verma et al., 2010).

Bio-energy is developed through biomass namely, wood, agricultural and municipal waste, bio fuels (liquids) like alcohol and various vegetable oils and their chemically modified derivatives. Bio-liquid fuels are more advantageous than solid fuels due to easy transportation. The vegetable oils and their chemical conversions are the most suitable substitutes for diesel fuel. Biodiesel is a biodegradable, nontoxic, acceptable alternative fuel, having strong correlation with sustainable development, energy conservation, management and environmental preservation (Agarwal, 2007).

1.2 Energy Scenario

Uneven distribution of petroleum and other fossil fuel reserves has been a great concern for developing countries like India. The total estimated production of crude oil in the world for years 2006-07, 2012-13 and 2015-16 has been about 3963.3 MT, 4119.2 MT and 4361.9 MT respectively (Energy Statics, 2017). As per the data given by Energy Statics 2017, Middle East Asia accounts for the highest share (32.38%) of total world production of petroleum during 2015-2016, followed by North America (20.87%), Europe & Eurasia (19.41%), Asia Pacific (9.14%), Africa (9.12%) and South & Central America (9.10%). Saudi Arabia and United States were the leading producers during 2015-16 with 13.03% and 13.0% share respectively, followed by Russia (12.40%), Canada (4.94%), China (4.92%), Iraq (4.52%), Iran (4.19%), UAE (4.02%), Kuwait (3.42%), Venezuela (3.1%), Brazil (3%), Mexico (2.92%) and Nigeria (2.59%). India accounted for 0.94% of the total world production. However consumption pattern reveals that India is the third largest and second largest crude oil consumer in the world and Asia-Pacific region respectively. USA tops the chart, consuming 19.66% of the total world consumption in 2015-16, followed by China (12.92%), India (4.51%), Japan (4.38%), Saudi Arabia (3.88%) and Russia (3.3%). Figure 1.4 and 1.5 shows region wise estimate of consumption and production of crude oil respectively in 2015-16.

The energy demand has shown a steep increase in India since 1991 globalization and industrialization reforms. India requires energy security to maintain high growth rate and economic development of the country. With continuously evolving energy systems over last six decades, ever increasing demand of energy has lead to remarkable pressure on its limited resources and has necessitated optimum use of its resources. The Indian energy policy is mainly defined by the country's escalating energy scarcity and increased attention on emerging alternative sources of energy. Indian economy is mainly agriculture based and modern agriculture system is heavily dependent upon internal combustion engines for running farm machinery, irrigation pump sets, and other equipments. Indian growth is mainly based on energy, produced by “oil-burning” in IC engines. Developing economy like India is a net importer of crude oil which stresses its foreign exchange reserves.

The estimated reserves of crude oil in India as on 31.03.2016 stood at 621.10 million tonnes (MT) against 635.60 million tonnes on 31.03.2015. The estimated reserves of crude oil decreased by 2.28% for India during 2015-16 as compared to 2014-15. India is highly dependent on import of crude oil. Net imports of crude oil have increased from 111.50 MTs during 2006-07 to 202.85 MTs during 2015-16. There has been an increase of 7.08% in the net imports of crude oil during 2015-16 over 2014-15, as the net import increased from 189.43 MTs to 202.85 MTs as shown in Figure 1.6. In the total production of Petroleum products during 2015-16, High speed diesel oil accounted for the maximum share (42.51%), followed by Motor Gasoline (15.23%) as shown in Figure 1.7.

As Indian economy is heavily based upon IC engines, it is not possible in any case to discard them and to use some other, easily available renewable fuels in India. These renewable fuels must be sought to lease new life to existing engines in order to curb the twin problems of fuel scarcity and air pollution. Various national emission standards have been set by the Government of India through which the fleets are facing greater pressures to switch to cleaner alternative fuels. The alternative fuels are desirable from the fact that they are the only fuels used with recent engine developments, which can meet the stringent EURO-VI emission norms.

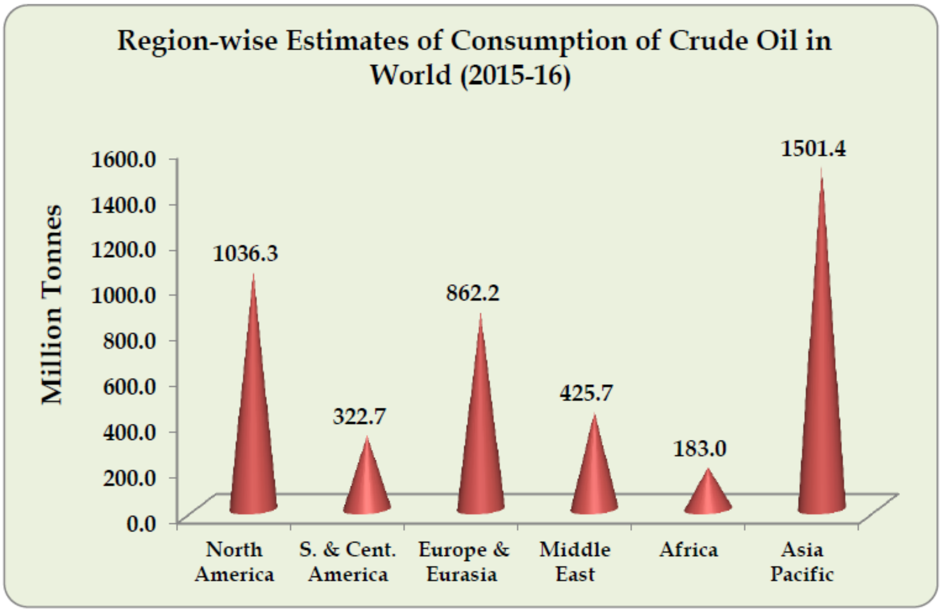


Fig. 1.4: Region wise estimate of consumption of crude oil in 2015-16 (Energy Statics, 2017)

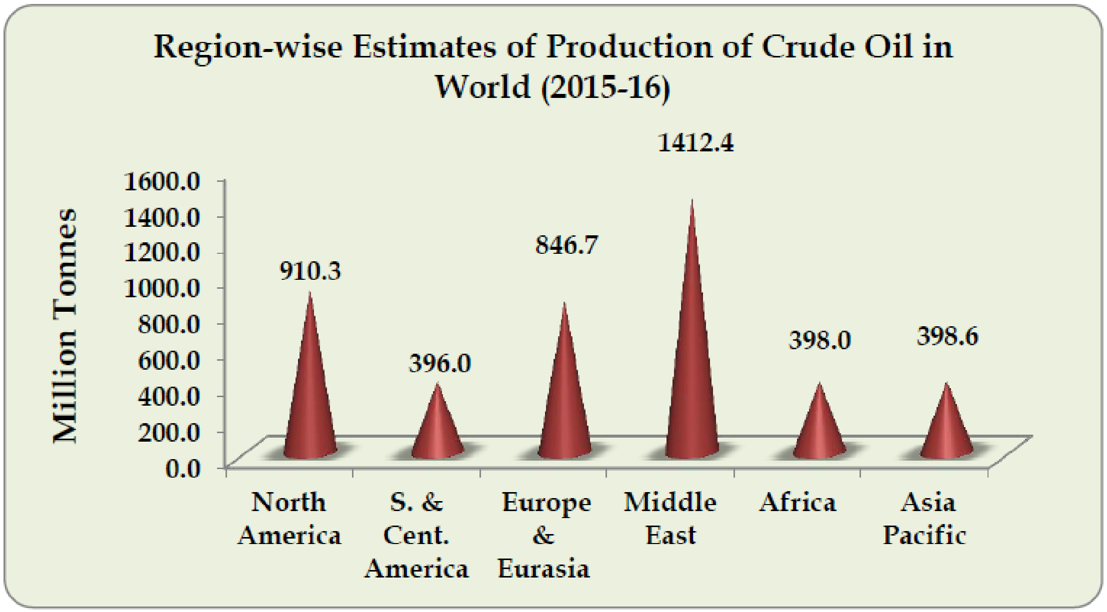


Fig. 1.5: Region wise estimate of production of crude oil in 2015-16 (Energy Statics, 2017)

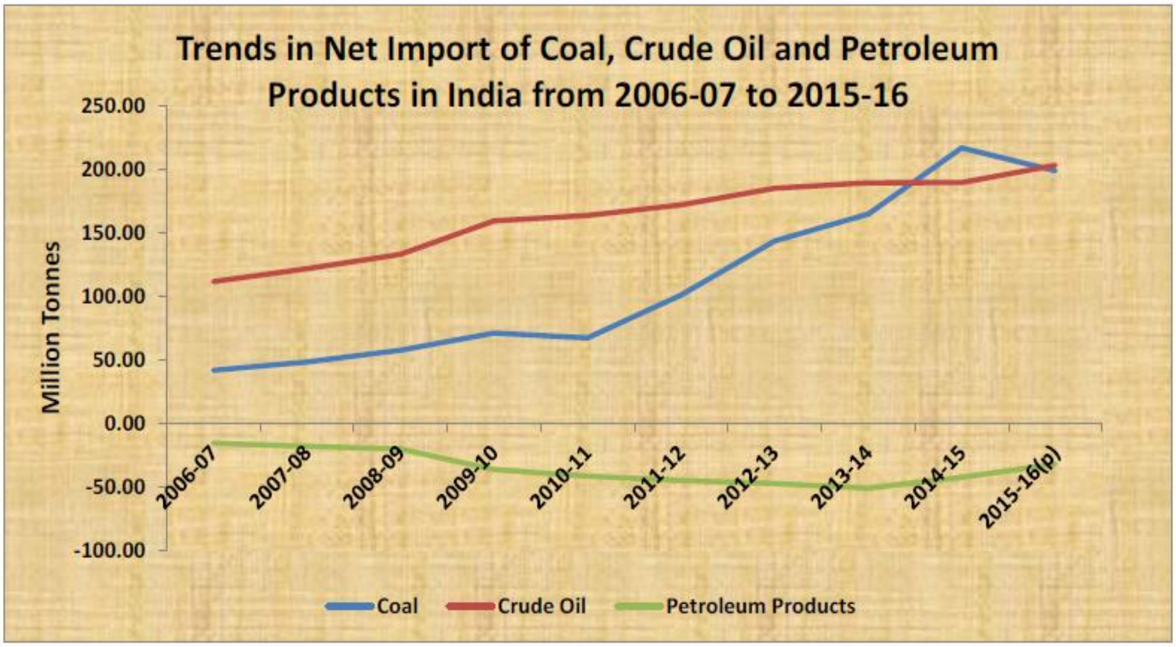


Fig. 1.6: Net Import of crude oil in India (Energy Statics, 2017)

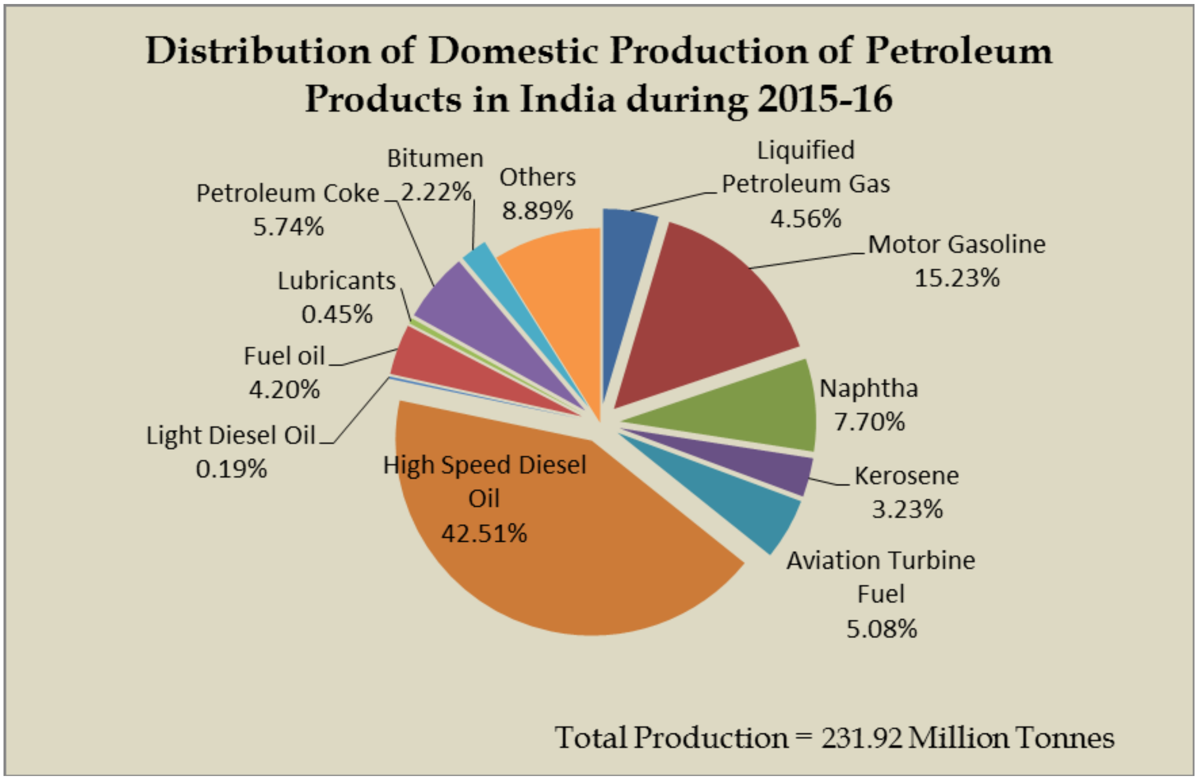


Fig. 1.7: Distribution of petroleum products production in India during 2015-16 (Energy Statics, 2017)

1.3 Environmental Effects

All the fuels are associated with direct cost (associated with purchase price of fuel) and externalities, the hidden cost of fossil fuels, which is not represented in market price. It involves the consequences associated with extraction, transportation and burning of fuels. The consequences are pollution, land degradation and human health detoriation. Costs accumulate at every step of the fossil fuel supply chain. Fossil fuel extraction generates air and water pollution, and harm local communities. Transporting fuels from the mine or well to the end user causes air pollution and may lead to severe accidents and spills. Burning fuel emits toxins and leads global warming emissions. Even the waste products are hazardous to public health and the environment. Emissions causing global warming are not only generated when the fuels are burnt, but oil drilling also produces methane which is generally vented to atmosphere. The green house effect of methane is much more severe than CO_2. In 2014, approximately 78 percent of US global warming emissions were energy-related emissions of carbon dioxide. Of this, approximately 42 percent was from oil and other liquids, 32 percent from coal, and 27 percent from natural gas (Energy Information Administration, 2016). Several global effects like ozone layer depletion, global warming, winter smog and acidification etc. are caused by CO, methane, non-methane hydrocarbons, nitrogen oxides etc which are liberated by burning of fossil fuels (Ministry of Petroleum and Natural Gas, 2009; Amoroso et al., 2006; Leveander, 1990). Renewable energy technologies like wind, solar, and geothermal energy, contributed less than 1 percent of the total energy related global warming emissions. Although fossil fuels contain large amounts of energy, they're contaminated and never found in pure form. Instead, they are typically refined and purified into a usable form, leaving behind hazardous waste which requires proper disposal. The handling and disposal of this waste is costly and causes environmental degradation and community health challenges.

1.4 Why Biofuels?

The IEA (International Energy Agency) characterizes energy security as "*the continuous accessibility of energy sources at a reasonable cost*". Attention must be paid on long term as well as short term security of energy. Price fluctuations depending upon supply and demand from oil market leads to the danger of physical inaccessibility with the financial harm caused by extraordinary price hike. Guaranteeing energy security has been the main objective of the IEA since its initiation. The newly incorporated policies of IEA are to find and develop alternative energy sources so that dependency on crude oil can be reduced. Liquid bio-fuels have potential to provide energy security for net oil importing developing countries. Agriculture based biofuel preparation in countryside regions is considered as a potential technique for rural economic development. Biofuel production from different feedstocks has the ability to generate new employment and create monetary spinoffs in countryside zones. This would be highly beneficial for agricultural bound developing nations. For all purposes of transportation, 94% growth of energy consumption is projected for developing countries by 2040 (U.S. Energy Information Administration | International Energy Outlook 2016). Nitrogen oxides (NOx), particulates matter (PM), sulfur dioxide (SO_2) and hydrocarbons (HC) are the major emissions from CI Engines, which are exhausted into atmosphere. Liquid biofuels which have the potential to substitute petro-diesel have been investigated all over the world. Burning liquid biofuels reduces the harmful emissions significantly.

1.5 Introduction to Biodiesel

Biodiesel has the potential to substitute mineral based petro-diesel due to its additional features like renewability, non toxicity, biodegradability and improved combustion performance characterstics (Barnwal et al., 2005; Li et al., 2005). Biodiesel constitutes of mono alkyl esters of fatty acids. These mono alkyl esters are produced by exchange of alkoxy group of natural triglycerides (such as vegetable oils, animal fats and waste lipids) by alcohol. American Society for testing materials (ASTM) defines biodiesel as the "*mono alkyl esters of long chain fatty acids derived from renewable liquid feedstock's, such as* *vegetable oils and animal fats, for use in compression ignition engines.*" The properties of vegetable oil must be altered so that it can be made compatible to the requirement of existing engines. The vegetable oils when reacted with alcohol, gets converted into alcoholic esters (biodiesel) which has almost same properties that of mineral based diesel (Demirbas, 2008). I.C. engines were first run on methyl and ethyl esters in France in 1940 but no significant proceedings were made until 1980, until high petroleum prices caused jitters across the world (Balat et al., 2008). In the 1980s and 1990s, significant research and development work was carried out for a variety of biodiesel feedstocks. Emissions analysis, I.C. engine performance and various economical methods of biodiesel production were studied. Biodiesel at any proportions can be mixed together with petro-diesel to form biodiesel blend or can be used in its pure form. Similar to petro-diesel, biodiesel is suitable for C.I. engines; which basically requires little or no modifications in the existing engine hardware because biodiesel possesses properties similar to petro-diesel. Moreover, biodiesel do not require separate infrastructure for its storage.

The use of biodiesel in straight diesel engines result in sizeable reduction of un-burnt hydrocarbons (HC), carbon monoxide (CO) and particulate matters (Agarwal et al., 2009). However its use increases nitrogen oxide (NO_x) to some extent. NO_x emissions can be prevented to get exhausted into atmosphere by using Exhaust Gas Recirculation (EGR) system. Biodiesel is considered as an uncontaminated fuel because of absence of sulphur and aromatics. Moreover it has about 10% built in oxygen, which aids in its complete combustion. However some of the shortcomings of biodiesel are: elevated viscosity, lesser heating value, higher freezing point and inferior flow properties at low temperature as compared to petro-diesel.

Table 1.1: Summary of proposed BIS standards for biodiesel (Li et al., 2005)

Property	Unit	Proposed BIS specification
Density @ 15°C	g/cm^3	0.87-0.9
Viscosity @ 40°C	mm^2/s	3.5-5
Flash point	°C	>=100
Sulphur content	%mass	0.035
CRR, 100% distillation residual max.	%mass	0.05
Sulphated ash, max	%mass	0.02
Water.max	mg/kg	500
Total contamination, max	mg/kg	20
Cetane no.		>=51
Acid no.	mg KOH/g	<=0.8
Methanol	%mass	<=0.02
Ester content	%mass	>=96.5
Triglyceride	%mass	<=0.2
Free glycerol	%mass	<=0.02
Total glycerol	%mass	<=0.25
Iodine no		<=115
Phosphorus	ppm	<=10
Alkaline matter (Na, K)		<=10

1.6 Feedstocks for Biodiesel

Biodiesel can be produced from triglycerides present in naturally occurring fats and oils by transesterification with alcohol, usually methanol or ethanol. Generally the transesterification is carried out in the presence of a catalyst for enhanced reaction rate. Feedstocks for biodiesel can be classified into “first-generation” and “second generation” feedstocks. First generation feedstocks include an edible portion of the above ground biomass (mostly grains and seeds) whereas second generation feedstocks include non-edible lignocelluloses residues of food crop or purpose-grown plants or grasses for energy, generally grown on wasteland and their cultivation cost is much less than that of edible vegetable crops. Currently more than 95% of the biodiesel produced globally is from edible vegetable oils because of its abundant production (Abbaszaadeh et al., 2012; Jianbing et al., 2006). The properties of biodiesel produced from these oils are much suitable to be used as a diesel fuel substitute (Gui et al., 2008). Moreover, edible vegetable oils have low Free Fatty Acid content and require a simple transesterification process for conversion into biodiesel. The feed stocks used for biodiesel production currently are high quality food grade vegetable oils, such as soya bean oil in U.S.A, Rapeseed oil in Europe, Palm oil in Malaysia, Coconut oil in Philippines (Agarwal et al., 2008).

Non edible vegetable oils are comparatively less popular due to their higher FFA content. A two-step transesterification process and longer time are required for their transesterification. Non-edible oil yielding plants can be grown on unproductive lands, degraded forests, cultivator’s fallow lands, irrigation canals and boundaries of road. Thus the use of non-edible vegetable oils will not jeopardize food supplies and biodiversities and therefore non-edible oils are considered as potential substitutes of edible food crops for biodiesel production. The more commonly used non-edible oils being exploited commercially are Jatropha, Karanjha, Mahua and Castor oil. However oils from Linseed, Sesame, Neem, Tobacco, Cotton seed, Rubber seed, Jaboba, Kapok etc are also investigated by many researchers across the world for production of biodiesel and performance testing (Balat et al., 2008; Silitonga et al., 2013, Abbaszaadeh et al., 2013; Moser et al., 2009). Other feedstocks include waste cooking oil, algae, agricultural waste and genitically modified plants.

1.7 Use of Vegetable Oil as Engine Fuel

Neat vegetable oils are not suitable as fuel for diesel engines. They have to be modified to bring their combustion-related properties closer to those of mineral diesel. This fuel modification is mainly aimed at reducing the viscosity to get rid of flow and combustion-related problems. Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of HC-based fuels. Vegetable oils can be used through at least four ways:

- ✓ Direct use and blending.
- ✓ Micro-emulsion.
- ✓ Pyrolysis (thermal cracking)
- ✓ Transesterification

Direct Use and Blending

Caterpillar (Brazil) in 1980 used pre-combustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alterations or adjustments to the engine. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% mineral diesel was successful. Some short-term experiments used upto a 50/50 ratio (Ma et al., 1999). Pramanik found that 50% blend of Jatropha oil can be used in diesel engine without any major operational difficulties but further study is required for the long-term durability of the engine (Pramanik et al., 2003). Direct use of vegetable oils and/or the use of blends of the oils have generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation, polymerization during storage and combustion, carbon deposits and lubricating oil hickening are obvious problems (Ma et al., 1999; Harwood, 1984)**.**

Micro-Emulsions

To solve the problem of the high viscosity of vegetable oils, micro-emulsions with solvents such as methanol, ethanol and 1-butanol have been investigated. A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimension generally in the 1–150 nm range, formed spontaneously from two normally immiscible liquids. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. Short term performance of micro-emulsions of aqueous ethanol in soybean oil was nearly as good as that of no. 2 diesel, in spite of the lower cetane number and energy content.

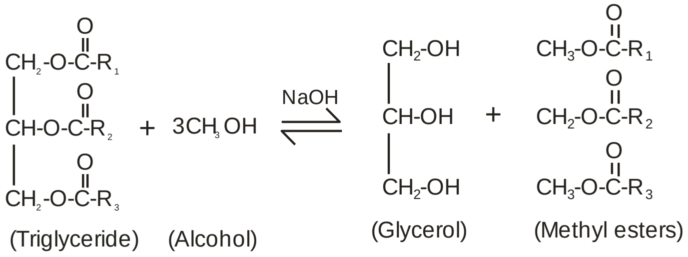
Pyrolysis (thermal cracking)

Pyrolysis is the conversion of one substance into another by means of heat or by heat in presence of a catalyst. The paralyzed material can be vegetable oils, animal fats, natural fatty acids or methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum.

Many investigators have studied the pyrolysis of triglycerides to obtain products suitable for diesel engine. Thermal decomposition of triglycerides produces alkanes, alkenes, alkadines, aromatics and carboxylic acids (Pramanik et al., 2003).

1.8 Biodiesel Production

The most cost-effective and generally used technique for biodiesel production is transesterification. The transesterification reaction between triglycerides and methanol to produce mono alkyl esters of fatty acids (biodiesel) and glycerol is shown in equation (1). This transesterification reaction involves uninterrupted intermixing of triglycerides and alcohol. Lower carbon alcohols such as Methanol and Ethanol are commonly used alcohol due to its economic feasibility and rapid reaction with triglycerides. Acidic catalysts are used for oils with high FFA content whereas much lesser corrosive alkali catalyst are preferred for low FFA feedstocks (Agarwal, 2007; Freedman et al., 1984).



$$\begin{array}{l} CH_2\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_1 \\ CH\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_2 \\ CH_2\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_3 \end{array} + 3CH_3OH \overset{NaOH}{\rightleftharpoons} \begin{array}{l} CH_2\text{-OH} \\ CH\text{-OH} \\ CH_2\text{-OH} \end{array} + \begin{array}{l} CH_3\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_1 \\ CH_2\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_2 \\ CH_3\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}R_3 \end{array} \quad (1)$$

Oils with FFA content greater than 2.5% requires a pretreatment process in presence of an acid before undergoing alkali catalyzed transesterification reaction. Yield of biodiesel produced from oils containing higher percentage of FFA is comparatively less than that of biodiesel produced from oils with lower FFA content. The most important variables affecting the yield of biodiesel from transesterification are:

- Reaction temperature
- Molar ratio of alcohol and oil
- Catalyst concenteration
- Reaction time
- Moisture and FFA content

Reaction Temperature

The time required for completion of transesterification reaction is strongly influenced by the reaction temperature. The reaction will progress close to completion even at room temperature. The optimum reaction temperature is found to be slightly below the boiling point temperature of methanol (60–70°C) (Ma et al., 1999; Pramanik et al., 2008, Freedman et al., 1984; Agarwal, 1998; Agarwal et al., 2001).

Molar Ratio

Molar ratio in which reactants: alcohol and vegetable oil are used, plays an important role in determining the transesterification rate. The stoichiometric molar ratio is 3:1 with 3 mole of alcohol required per mole of triglyceride to yield 3 mole of fatty esters and 1 mole of glycerol. Transesterification is a reversible reaction and in order to swing the transesterification reaction to the right, use of excess alcohol is recommended. Use of 100% excess methanol is recommended, to achieve highest reaction rate and optimum yield for feedstocks obtained from edible oils (Freedman et al., 1984).

Catalyst Concenteration

Catalysts are broadly classified into alkali and acidic catalyst. Another category is that of biological catalyst, known as enzymes. Alkali-catalyzed transesterification is comparatively more rapidly than acid-catalyzed reaction. However, high FFA and high moisture content vegetable oils, are better transesterified with acid catalysts. Rapid esterification and lower corrosive action on industrial equipments makes alkaline catalysts favourable for commercial use (Freedman et al., 1984; Agarwal, 1998)

Reaction Time

The conversion rate increases with reaction time (Ma et al., 1999; Freedman et al., 1984).

Moisture and FFA content

For an alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. The soap lowers the yield of esters and renders the separation of ester and glycerol and water washing difficult. The glycerol is then removed by gravity separation and remaining ester is mixed with hot water for separation of catalyst. Moisture can be removed using silica gel. Ester formation eliminates almost all the problems associated with vegetable oils. Saponification reaction also takes place simultaneously along with transesterification process but soap formation is not a major problem if presence of water is less than 1% (Ma et al., 1999; Pramanik et al., 2008, Freedman et al., 1984; Agarwal, 1998; Agarwal et al., 2001). Starting materials used for alkali-catalyzed transesterification of triglycerides must meet certain specifications. The glyceride should have an acid value less than 1 and all reactants should be substantially anhydrous. If the acid value was greater than 1, more NaOH is required to neutralize the FFA. Freedman et al. found that ester yields were significantly reduced if the reactants did not meet these requirements. Sodium hydroxide or sodium methoxide reacted with moisture and carbon dioxide in the air, which diminished their effectiveness (Freedman et al., 1984). The effects of FFA and water on transesterification of beef tallow with methanol were investigated by Ma and Hanna (Ma et al., 1999). The results showed that the water content of beef tallow should be kept below 0.06% w/w and free fatty acid content of beef tallow should be kept below 0.5%, w/w in order to get the best conversion. Water content was a more critical variable in the transesterification process than FFA (Ma et al., 1999).

Intermixing of reaction mixture can be done in the following ways:

Mechanical Stirring

In the process mixing of oil and alcohol is carried out by a motor operated mechanical stirrer. This is most commonly used conventional technique. It has limitations of higher reaction time and capacity. Usually it is time consuming and may be used only for small capacity biodiesel production.

Hydrodynamic Cavitation

In hydrodynamic cavitation method mixing of two phases of reactants is carried out by cavitation conditions, produced by pressure variation, which in turn obtained by using the geometry of system to create velocity variation. Cavitation is generated by the flow of liquid under controlled conditions through simple geometries such as venturi tubes & orifice plates. When the pressure at the throat falls below the vapour pressure of the liquid, the liquid flashes, generating a large number of cavities which subsequently oscillates and then give rise to the pressure & temperature pulses. These pulses cause the better mixing of immiscible liquids and enhanced transesterification process (Pal et al., 2010).

Ultrasonic Cavitation

Principle of ultrasonic cavitation method is based on the process of creating cavities in the fluid by the irradiation of power ultrasonic with sufficient energy in immiscible liquid (oil and alcohol are immiscible with each other). As a result micro fine bubbles are formed and these bubbles are collapsing at various places of the reactor and disturb the phase boundary between two immiscible liquids and it results in emulsification of the mixture. Energy liberation of the order of 1 to 10^{18} kW/m^3 during ultrasonic cavitation process raise the overall temperature of reaction mixture upto a level required to carry out transesterification reaction eliminating the need of external heating agency (Gogate et al., 2005; Lee et al., 2011).

1.9 Properties of Biodiesel

The significant biodiesel properties are cetane number, density (kg/m^3), viscosity (mm^2/s), cloud and pour points (°C), flash point (°C), acid value (mg KOH per g-oil) and oxidation stability. The physical and chemical properties vary from one type of feedstock to another and their fatty acids composition (Atadashi et al., 2010; Lin et al., 2009).

Kinematic viscosity

The viscosity of fluid is the measure of resistance offered to flow. Higher is the viscosity, lower is the fluidity of the fuel (Demirbas, 2009). Viscosity is also a strong function of temperature and biodiesel becomes highly viscous or may even get solidified at low temperatures. It can be concluded from the past studies shows that high viscosity adversely affect the volume flow rate and injection spray features in the engine. The acceptable range of kinematic viscosity is 3.5-5 mm^2/s as per EN ISO 3104 standards (Murugesan et al., 2009).

Density

The quantity mass per unit volume is known as density. Density is important in determining the delay between the injection and combustion of the fuel in a diesel engine. Density of biodiesel can be evaluated using ASTM D1298 test method.

Flash point

Flash point of a liquid fuel is its lowest temperature at which the fuel vapours form an ignitable mixture with air near the free surface of liquid fuel. Lower flash points represents the ease to ignite the fuel. Flash point has an inverse relation with the volatility. The flash point of biodiesel is about 150 °C which is much higher than flash point of conventional petro-diesel (55-60°C). This makes transportation, handling and storage of biodiesel much safer than that of diesel (Atadashi et al., 2010; Murugesan et al., 2009).

Pour point, Cloud point and cold filter plugging point

The resistance to flow increases with decrease in temperature. A temperature will come where the liquid losses its flowability. This temperature is called pour point (PP). Temperature at which wax crystals primarily becomes noticeable upon cooling the fuel in a test model is known as cloud point (CP). Pour point and cloud point of biodiesel is somewhat greater than that of diesel (Demirbas, 2009) and are measured using ASTM D2500 and D97 test methods (Demirbas, 2005). Cold filter plugging point (CFFP) represents the filterability limit of fuels. Test method ASTM D6371 is used to calculate CFPP (Murugesan et al., 2009)

Cetane number

Cetane number (CN) shows a direct relation with chain length of fatty acids and the level of saturation. CN strongly affects the delay period and ignition quality. (Balat, 2011). Higher

CN represents shorter delay period and smoother combustion with improved efficiency. A great advantage of biodiesel over petro-diesel is its higher CN (Lapuetra et al., 2008).

Oxidation stability

The class of biodiesel produced can be determined from its oxidation. Oxidation stability represents the degree of oxidation, potential reactivity with air. Lower is the oxidation stability, more is the need of antioxidants. Double bonds in the fatty acid chains represent the site for reaction with oxygen, which is a highly undesirable phenomenon (Atadashi et al., 2010). The Rancimant method (EN ISO 14112) is registered as the oxidative stability specification in ASTM D6751 and EN 14214.

Acid value

The amount of carboxylic acid groups present in a chemical compound is represented by Acid Value. Higher is the FFA amount, higher is the acid value. It is represented as amount of KOH required in mg for complete neutralizing 1 gm of FAME. EN 14104 and ASTM D664 are used to decide the acid value of biodiesel.

1.10 Organization of Thesis

This thesis is made up of nine chapters. The organization of the chapters is listed as follows:

Chapter 1 deals with the current energy scenario of India and world, concerns related to energy security and environmental pollution due to lavish extraction of fossil fuels. Scope of biodiesel as an alternative to petro diesel and its relative merits and demerits are discussed further. Some important physical and chemical properties of the biodiesel are highlighted. Various methods to use vegetable oils in CI engines are also analyzed along with different techniques of transesterification.

Chapter 2 deals with the literature review in which research articles related to biodiesel production are summarised. This section highlights the research conducted by various scientists which gave the guidelines for the present research work. Literature Rivew is classified into 5 broad categories: Raw materials for biodiesel production, Optimization of reaction parameters, Conventional and Non-Conventional techniques of biodiesel production, Economic and enviourmental aspects of biodiesel and stability of biodiesel.

Chapter 3 explains the research methodology. First of all exhaustive literature review was done. From the gaps in literature review, it was analysed that experiments have been performed on small scale laboratory size setups. We developed closed loop combined process biodiesel reactor for large scale production with focus on cavitation techniques. Various process parameters were altered to obtain optimal conditions for biodiesel production. Main criteria in search of alternative oils are their availability, ease of extraction and FFA content.

Chapter 4 deals with optimization of various process parameters of biodiesel production through ultrasonic cavitation for laboratory scale batch type production. Biodiesel production is carried out in ultrasonic horn reactors, ultrasonic bath reactors, double frequency flow cell reactor and triple frequency hexagonal flow cell reactor. Triple-frequency flow cell reactor is found to be the most energy-efficient ultrasonic reactor for biodiesel production in terms of Specific Energy Consumption and Energy Use Index.

Chapter 5 deals with construction of closed loop combined process biodiesel production reactor and optimization of various process parameters of biodiesel production. Combined

Process Reactor has minimum Specific Energy Consumption, minimum requirement of methanol to oil molar ratio and minimum catalyst requirement when compared with closed loop ultrasonic reactor and mechanical stirrer.

Chapter 6 deals with optimization of various process parameters of biodiesel production through ultrasonic cavitation under pressurized conditions. Lower requirement of catalyst and alcohol to oil molar ratio, lower energy consumption, higher value of EUI, simpler purification of products and rapid reaction rate at 15-20 bar pressure of reaction mixture makes it the most economically viable condition for biodiesel production.

Chapter 7 deals with economic feasibility of biodiesel production

Chapter 8 discusses the conclusion of the thesis from the research work and possible direction for further research.

CHAPTER 2

LITERATURE REVIEW

This chapter deals with reviews of some noteworthy research articles which provided in depth understanding about the research area.

2.1 Raw Materials

Agarwal et al., 2012, investigated edible and non edible oils from various feedstocks to prepare biodiesel using KOH as catalyst and methanol as alcohol. The optimal conditions for maximum biodiesel yield from all vegetable oils was obtained under following conditions: reaction temperature 70 °C; reaction time 1 h; catalyst concenteration 1% (by oil wt.); and methanol to oil (M:O) molar ratio 6:1. Characterstics of biodiesel prepared at optimum conditions was found to comply with ASTM standards.

Endalew et al., 2011, investigated transesterification of high free fatty acid (FFA) Jatropha curcas oil (JCO) into biodiesel using heterogeneous catalyst. Solid base and acid catalysts were formed and used for biodiesel production in a batch reactor under suitable reaction conditions. Combination of solid base and acid catalysts were also used for one-step concurrent esterification and transesterification. Formation of soap was the major problem associated with use of calcium oxide (CaO) and lithium doped calcium oxide (Li-CaO) catalysts during the transesterification of jatropha oil. This problem was found to be comparatively much lesser with transesterification of rapeseed oil (RSO). CaO when doped with Li demonstrate greater conversion to biodiesel as compared to bare CaO as a catalyst.

La_2O_3 /ZnO, La_2O_3 /Al_2O_3 and $La_{0.1}Ca_{0.9}MnO_3$ catalysts were also tested. Use of La_2O_3-ZnO gave much better results due to enhanced activity.

Tang et al., 2011, investigated the use of CaO modified by trimethylchlorosilane (TMCS) as catalyst for transesterification of rapeseed oil to its methyl esters. Fatty acid methyl esters (FAME) yield showed a significant increase in yield from 85.4% to 94.6% by use of modified CaO. This improved yield is due to enhanced absorption of grease on modified catalyst surface. Verified results after repeated experiments prove that the modified catalyst is water resistance and can be reprocessed for multiple runs without showing sign of any reduction in activity. Humidity test in the vapor-saturated atmosphere is used to verify the result. Characterization of the catalyst was made and the effects of various process parameters such as catalyst concenteration, reaction temperature and M:O molar ratio were investigated.

Kiakalaieh et al., 2013 investigated waste cooking oil (WCO) transesterification into biodiesel using heterogeneous heteropoly acid (HPA) catalyst. The effect of different process parameters such as M:O molar ratio, catalyst concenteration, reaction temperature, and reaction time were estimated. The maximum yield of 88.6% was obtained at the optimal reaction condition of 70:1 M:O molar ratio, 65°C reaction temperature, 10 wt% catalysts, and 14 h reaction time. The catalyst showed enhanced activity, reusability upto a minimum of four times and easy separation. The catalyst considerably reduced the cost of pre-treatment, separation and purification processes.

Dibakar et al., 2010, investigated transesterification of Yellow oleander (Thevetia peruviana Schum) seed oil to produce biodiesel by use of methanol in a batch reactor. Researchers used heterogeneous catalyst derived from the trunk of Musa balbisiana Colla (one variety of banana plant). Biodiesel yield of 96 wt. % was obtained at 32 ^{0}C in 3 h. The biodiesel produced constitutes of methyl oleate 43.72%, methyl palmitate 23.28%, methyl linoleate 19.85%, methyl stearate 10.71% and methyl arachidate 2.41%. Fuel properties tested were in accordance with ASTM D6751, EN 14214, BS II and BS III test standards. The biodiesel so produced was found to be free from sulfur and has showed a high value of cetane number (61.5).

Mandeep et al., 2011, prepared Lithium impregnated calcium by wet impregnation method in nano particle form as supported by powder X-ray diffraction and transmission electron microscopy. Lithium impregnated calcium oxide Calcium (with 1.75 wt% of lithium) was used as heterogeneous catalyst for the biodiesel production from high FFA karanja and jatropha oil. The oils contained 3.4 wt % and 8.3 wt % of FFA, respectively. The various process parameters such as reaction temperature, M:O molar ratio, FFA content, catalyst concenteration and quantity of lithium ion to be impregnated have been evaluated for the optimal conditions of biodiesel conversion. Reaction time for complete transesterification of karanja and jatropha oils was found to be 1 and 2 h respectively with reaction temperature maintained at 65°C, M:O molar ratio of 12:1 and 5 wt% catalyst concenteration.

Zanette et al., 2011, investigated the biodiesel production from Jatropha curcas oil using various heterogeneous catalysts such as resins, zeolites, clays, hydrotalcites, aluminas and niobium oxide. The screening of KSY clay and Amberlyst 15 catalysts was done in a batch reactor for the following values of process parameters: M:O molar ratio of 1:9, 6 h of reaction and 5 wt% catalyst concenteration. A 2^3 full factorial central composite rotatable design was formed to evaluate the effects of process variables on biodiesel conversion. The most favourable conditions for both catalysts were 1:12 M:O molar ratio, 5 wt% of catalyst, 433 K and 6 h of reaction time with biodiesel yield of 70 wt%. Semi-empirical model was developed and kinetic study was performed to represent the experimental data. Ultimately, catalyst was reused for five successive batch experiments under optimized reaction conditions.

Devanesan et al., 2007, carried out conversion of vegetable oils into fatty acid methyl and ethyl esters. Biodiesel preparation with the use of commercially immobilized *Pseudomonas fluorescens* MTCC 103 catalyst under mild transesterification reaction conditions from Jatropha oil was carried out. The cell of *P. fluorescens* was easily immobilized within the sodium alginate during batch process. The various process parameters like reaction temperature, pH, M:O molar ratio, amount of beads and reaction time were investigated with optimal values of 40ºC, 7.0, 4:1, 3 g bead and 48 h reaction time respectively. The physio-chemical properties of biodiesel were evaluated and compared with that of petro-diesel. Biodiesel so produced was found to be suitable for use in existing diesel engine without any alterations in engine.

Alhassan et al., 2014, investigated cotton seed oil (CSO) conversion into biodiesel through transesterification by use of various mixtures such as methanol with Diethyl Ether (DEE) or with Dichlorobenzene (CBN) or with Acetone co-solvent. Potassium hydroxide (KOH) was the catalyst used to enhance the rate of transesterification for all the experiments. The process variables viz. molar ratio of co-solvent in methanol, reaction temperature, reaction time and catalyst concenteration were optimized to obtain maximum yield of FAMEs. Co-solvent addition favourably affected the reaction time and moreover it also various properties of the biodiesel produced.

Lapuetra et al., 2008, experimentally investigated and compared the performance of methyl and ethyl ester of waste cooking oil in a 2.2 l, common-rail injection diesel engine. Pure biodiesel fuels (in comparision with reference fuel) resulted in a small rise in fuel consumption and NO_x emissions and a substantial decrease in total hydrocarbon (THC) and particulate emissions (PM) and smoke opacity. Alcohol used in transesterification also affected the emissions and PM composition. More volatile alcohols resulted in increase of THC emissions as well as volatile organic fraction of the particulate matter.

Zanuttini et al., 2014, investigated production of alkyl esters from Butia Yatay coconut oil having an acid values between 109 and 140 mg KOH/g. The raw coconut oil underwent a three-step degumming pre-treatment process to decrease the phosphorus content from 600 ppm to approximately 200 ppm. Kinetic study of important concurrent reactions such as autocatalysis, triacylglycerides hydrolysis, transesterification, and the reaction of sulphuric acid with the alcohol was done. The kinetic constant for the esterification reaction was found to be a function of time and has a inverse relation with it, because of continuous catalyst consumption in alkyl-sulphate formation reaction.

Joshi et al., 2015, investigated transesterification of high FFA Jatropha and Karanja oil using CaO based metal oxides (M-CaO; ZnO, MnO_2, Fe_2O_3 and Al_2O_3) as heterogeneous catalyst. The catalysts so prepared were compared for their catalytic performance (which has a strong correlation with calcination temperature) and their characterizations were done by XRD, SEM, TGA, FT-IR and BET techniques. ZnO–CaO has the highest catalyst activity among all catalyst. Maximum biodiesel yield from Jatropha and Karanja oils were obtained for the following reaction parameters: 5 wt% catalyst concenteration, 65°C reaction temperature and 12:1 M:O molar ratio.

2.2 Conventional and Non-Conventional Techniques of Biodiesel Production

Noiroj et al. [2009] has investigated the use of KOH/Al_2O_3 as heterogeneous solid base catalysts for transesterification of vegetable oil by use of conventional mechanical stirring process. The optimal values for reaction parameters were 2h reaction time, 25 wt. % catalyst concenteration, 15:1 M:O molar ratio, stirring speed of 300 rpm and 60°C reaction temperature with a maximum biodiesel yield of 91.07%.

Li et al. [2009] investigated transesterification of low-cost ESG oil by use of solid heteropolyacids Cs2.5H0.5PW12O40 catalyst in small scale lab size reactor using mechanical stirring. Very high biodiesel yield of 99% was obtained with M:O molar ratio of 6:1, reaction time (12 h) and reaction temperature (65°C) with low catalyst requirement.

Janajreh et al. [2016] evaluated conventional and ultrasonic assisted process for biodiesel production and compared the reaction kinetics and biodiesel yield with both processes. Transesterification assisted with ultrasonic irradiation was found to be more effective than conventional process with lower requirement of M:O molar ratios in sonicated process.

Maeda et al. [2007] investigated the conversion of vegetable oil with the help of low frequency ultrasonic irradiation (40 kHz). The fatty acid methyl ester concenteration of mono, di and tri glycerides of the actual reaction mixture was evaluated for short reaction time by HPLC. Small amount of diglycerides and large amount of monoglycerides were found which showed that the last step of transesterification is relatively slow in comparision to initial phase of transesterification.

Hanh et al., 2008, investigated biodiesel production from triolein by irradiation of low frequency ultrasonics (40 kHz) at room temperature (25°C) using KOH catalyst and compared the results with that of traditional mechanical stirring technique of biodiesel production. Further he found the optimum conditions (such as molar ratio, catalyst concentration and reaction time) of the methanolysis reaction. Biodiesel yield was found to increase sharply with increase in Methanol to Triolein molar ratio from 3/1 to 6/1 and thereafter holds constant with further increase in molar ratio. Biodiesel yield was found to increase with increase in catalyst concentration from 0.5% to 1% and then decreased from 1% to 3%. Further it was observed that biodiesel yield increased rapidly at a reaction time less than 10 min and then gradually increased to maximum at 30 min, and then holds constant with increasing irradiation time. The optimum condition of molar ratio, catalyst concentration and reaction time were observed to be 6/1, 1.5 wt% and 4 h, respectively under stirring conditions.

Haan et al., 2009, investigated biodiesel production from triolein using various primary and secondary alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-hexanol, 2-hexanol, 1-octanol, 2-octanol and 1-decanol) at 6/1 alcohol to triolein molar ratio and 25^0C in presence of base catalyst under ultrasonic irradiation (40 kHz) and mechanical stirring (1800 rpm) conditions. Biodiesel yield was found to increase sharply upto 10 mins of irradiation time with optimum yield obtained at 15 mins for all type of alcohols. Transesterification with short chain alcohols (methanol and ethanol) results in higher yield as compared to other long chain primary alcohols. Moreover, transesterification with secondary alcohols showed little ester conversion with an optimum yield of 3 % even under ultrasonic irradiation conditions. It is also shown that biodiesel yield (with all types of alcohols) under ultrasonic irradiation conditions were significantly higher than that under mechanical stirring conditions.

Gogate et al., 2006, overviewed the intensification of physical and chemical processing applications by ultrasonic and hydrodynamic cavitation phenomena and suitability of various cavitational reactors to carry out specific cavitational transformations. Biodiesel yield was found to increase sharply upto 10 mins of irradiation time with optimum yield obtained at 15 mins for all type of alcohols. Transesterification with short chain alcohols (methanol and ethanol) results in higher yield as compared to other long chain primary alcohols. Moreover, transesterification with secondary alcohols showed little ester conversion with an optimum yield of 3 % even under ultrasonic irradiation conditions. It is also shown that biodiesel yield (with all types of alcohols) under ultrasonic irradiation conditions was significantly higher than that under mechanical stirring conditions.

Gude et al., 2013, investigated the transesterification of waste cooking oil by ultrasonic irradiation technique. Effects of ultrasonic density, energy density, reactor design and thermal aspects of ultrasonics in transesterification reaction were studied. Further, the process parameters such as methanol to oil molar ratio, catalyst concentration and reaction time were optimized to obtain maximum biodiesel yield under ultrasonic irradiation conditions for a small sample size of 10 ml. Biodiesel so produced was tested for its properties and stability. High ultrasonic intensities of 50-500 W/cm^2 are suitable for biodiesel production using ultrasonic bath reactors. Maximum biodiesel yield is obtained for ultrasonic intensity of 123 W/cm^2. It was observed that 150 ml reactor has produced maximum biodiesel yield (86.5%) compared to others (61.2% for 50 ml, 81.3% for 100 ml and 80.5 % for 250 ml reactor). This is attributed to the fact that high temperatures obtained for small size reactors resulted in evaporation of methanol where as large cavitational zones for large size reactors resulted in decrease of biodiesel yield. The maximum biodiesel yield (90%) was obtained 0.5% catalyst, 9/1 molar ratio and 1-1.5 min reaction time.

Baddy et al., 2013, investigated the transesterification of Jatropha oil by ultrasonic irradiation technique using carbon supported tungstophoric acid catalyst. Ultrasonic process reactor capable of generating the frequency of 20 KHz with a highest power of 400W was utilized for biodiesel production. Variation of biodiesel yield with reaction variables such as reaction time, alcohol to oil molar ratio and catalyst amount were investigated for varying ultrasonic amplitude (30-90% of the maximum sonifier power) to find optimal conditions of biodiesel production. Optimal biodiesel yield of 91% was obtained in 40 mins reaction time for molar ratio of 25:1 and reaction temperature of 65°C. Biodiesel yield was also plotted against varying power of ultrasonic amplitude and it was found that biodiesel yield increases initially with increase in ultrasonic amplitude percentage, until it reaches the maximum value at amplitudes of about 60-70% and decreased beyond these levels. At higher ultrasonic power, cavitation bubbles starts combining to form a larger and stable bubbles which leads to poor penetration of ultrasonic energy in the reaction mixture and ineffective mixing of immiscible reactants

Ji et al., 2006, investigated alkali catalyzed biodiesel production from soybean oil under ultrasonic irradiation (19.7 kHz) conditions and orthogonal experiments were conducted to find optimal parameters for biodiesel production for the following reaction variable: power (100, 150 and 200 W), molar ratio (3:1, 4.5:1 and 6:1), pulse frequency (0.4, 0.7 and 1.0) and temperature (25, 35 and 45°C). Energy consumption for conversion of 1 kg soybean oil into biodiesel is compared for the MS, PU and HC methods of transesterification for the following reaction conditions: molar ratio 6:1; temperature 45°C;

KOH amount 1 wt.%; MS: speed 900 rpm; PU: 0.7 pulse frequency and 150 W power; HC: operation pressure 0.7 MPa; single orifice. Acid Value of soybean oil is 0.2. Optimal conditions for transesterification of soybean oil under ultrasonic irradiation conditions are: MR 6/1, temperature 45°C, continuous ultrasonics and 150 W ultrasonic power with almost 100% yield in 10-20 mins. However the energy consumption for PU was calculated for pulse frequency of 0.7 which is an efficient way to save energy. But as pulse frequency was lower than 0.7, macro-stirring effect of the ultrasonic was too mild to mix the immiscible reactants well. It was also investigated that ultrasonic power of 200 W resulted in decrease of FAME content due to formation of stable and larger bubbles. Energy consumption was 183 Wh/kg with HC as compared to 250 Wh/kg with PU and 500 Wh/kg with MS. Both HC and PU attained an yield of 100% in 10 mins and 30 min respectively for the above stated conditions.

Chadda et al., 2012, investigated and compared the biodiesel yield from jatropha oil through conventional and ultrasonic cavitation techniques. 31. 2% oil was extracted from crushed seeds (20 gm) in a soxhlet apparatus using hexane (200 ml) as solvent for 8 hr. The reactants used for transesterification are: 20 gm crushed seeds, methanol and NaOH. A sonicated probe of 20 kHz frequency and 750 W power was used for ultrasonic irradiation at room temperature. Conventional transesterification is carried out in a 500 ml reaction flask fitted with mechanical stirrer, condenser and a thermometer pocket. Properties of Jatropha oil are tested and found to be: density, 910 kg/m^3; viscosity at 40°C, 37.0 mm^2/s; acid value, 3.7 mg KOH/gm; iodine value, 99; oxidative stability, 2.56 h; cloud point, 8°C; pour point, 3°C and moisture content, 0.15%. Effect of varying jatropha seed to alcohol molar ratio (1:8, 1:10, 1: 12.5, 1: 15 w/v) and catalyst concentration (0.3-1.50%) were also studied to optimize biodiesel production. Biodiesel yield of 94.1% yield was obtained for biodiesel production through ultrasonic irradiation for the following reaction parameters: molar ratio 1:10 w/v, catalyst concentration 1% and reaction time 80 mins. Maximum yield of 80% was obtained for conventional transesterification in 5 h for the above optimized reaction parameters.

Hanh et al., 2009, investigated transesterification of Free Fatty Acids such as oleic acid, Palmitic acid and Stearic acid with short chain alcohols (ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol) in the presence of H_2SO_4 catalyst under ultrasonic irradiation conditions. Experiments were conducted to find optimal parameters for biodiesel production for the following reaction variables: temperature (10-60°C), molar ratio (1/1-10/1), catalyst amount (0.5-10% w/w of oil) and reaction time (0 to 10 hr). Analysis of biodiesel yield as a function of ethanol to oleic acid molar ratio shows that ethyl ester conversion increases rapidly with increase in molar ratio upto 3/1 and then decreases gradually under following reaction parameters: 5% catalyst and 20°C temperature. Analysis of ethyl ester yield as a function of catalyst concentration (reaction parameters: molar ratio and 20°C temperature) shows that there is a significant increase in yield with increase in catalyst amount from 0.5% to 5 % w/w of oil. However the increase in ethyl ester yield is marginal beyond 5% increase in catalyst concentration. Further it is concluded that optimum temperature of ethyl ester yield is 60°C for molar ratio 3/1 and 5 % catalyst concentration. All the above analysis showed that optimum yield is obtained at 2 h reaction time irrespective of reaction parameters. It is also seen that short and normal chain alcohols resulted in higher reaction rates when compared to long and secondary chain alcohols.

Starvarache et al., 2005, investigated transesterification of edible vegetable oil (Acid value 1.247 and Iodine value 70) with short chain alcohols (methanol, ethanol, Iso-propanol, Iso-butanol and Tertiary-butanol) in the presence of base catalysts (NaOH and KOH) by means of low frequency ultrasound (28 and 40 kHz). Effect of varying catalyst concentration (0.5%, 1% and 1.5%) was studied on the biodiesel yield for fixed molar ratio of 6:1. Secondary alcohols (Iso-propanol and Iso-butanol) showed some conversion under ultrasonic irradiation, while under stirring conditions no transesterification takes place. Tertiary alcohols have no conversion in any of the process. This may be due to the Stearic hindrance that impedes the access towards the reaction center.

Pal et al., 2010, investigated biodiesel production from Thumba oil through hydrodynamic cavitation using 4 orifice plates with 1, 3, 5 and 7 numbers of holes of 3 mm each. Transesterification is carried out with methanol to oil molar ratio of 4.5:1, 1% NaOH w/w of oil and reaction temperature of 45-55°C. B-10, B-20, B-30 blends of Thumba biodiesel were tested for variation of torque, brake power, BSFC, BTE and opacity with respect to engine speed on a four cylinder , direct injection water cooled diesel engine. Production of biodiesel from Thumba oil through transesterification showed that yield increases with increase in number of holes and after 30 minutes it remained almost constant for all types of orifice plates. Almost 80% biodiesel yield was obtained within 30 mins. For all the biodiesel blends and pure diesel, torque increases sharply upto engine speed of 2500 rpm, remains almost constant between 2500 and 4000 rpm and then shows the downward trend with further increase in engine speed. Brake power increases from 10 kW to 30 kW with increase in speed from 2000 to 4000 rpm for all biodiesel blends and pure diesel. Slight variations are shown in trend of brake power for biodiesel blends with increase in engine speed beyond 4000 rpm. Maximum brake power achieved is 35 kW at 5000 rpm for B-10 biodiesel blend. BSFC initially decreases sharply with increase in engine speed upto 2000 rpm, them remains almost uniform till 4000 rpm and then increases sharply beyond 4000 rpm for all the biodiesel blends and pure diesel. BSFC decreases with increase in biodiesel percentage and lowest BSFC is obtained for B-30 blend in the rpm range of 2000-4500. BTE shows almost an opposite trend to that of BSFC with maximum BTE of 26.5% achieved at 2000 rpm for B-30 blends. A general trend of increase in opacity was observed with increase in engine speed, with no significant change in its value beyond 4000 rpm for all types of blends and pure diesel. Opacity for pure diesel is slightly higher than biodiesel blends.

Guerra et al., 2015, investigated comparison of biodiesel production from used cooking oil for continuous and pulse ultrasonic irradiation. Parameters analysed for comparison were: Molar ratio (4.5/1, 6/1, 9/1, 13.5/1), Catalyst concentration (0.5, 1.25 and 2% w/w of oil), Reaction temperature, Reaction time (0.5-2.5 min), Ultrasonic power density and Ultrasonic intensity. A sample of 10 ml oil was used to conduct experiments, expect for ultrasonic power density, where sample were tested for 10, 20 and 30 ml quantities. A sample of 20 ml oil was taken to evaluate the effect of ultrasonic intensity for reactor size of 50, 100, 150 and 200 mL. 4 different molar ratios were tested for biodiesel production with other process parameters maintained at 1.25 % catalyst, 2 min reaction time and a power output of 150 W. 3 different catalyst concentrations were tested for molar ratio 9:1, reaction time 2 min and power output of 150 W. Parameters fixed to study the effect of power density are: 9/1 molar ratio, 0.5% catalyst and 2 min reaction time. Optimal yield of 96.8% and 81% are obtained for pulse and continuous sonication respectively at

9:1 molar ratio. Optimal yield of 96.8% was obtained for pulse sonication at 1.25% catalyst. Optimal yield of 81% was obtained continuous sonication at 0.5% catalyst. A higher catalyst concentration adversely affects biodiesel yield in continuous sonication due to excessive soap formation. Over excitation of the reactants in continuous sonication and the emulsification of reaction compounds causes difficulty in product separation in continuous sonication. Optimum yield of 98% was obtained at 2.5 min for pulse sonication as compared to 91% yield at 1 min obtained for continuous sonication. Yield started decreasing beyond 1 min for continuous sonication. Upto 60°C temperature was recorded at 1 min reaction time beyond which there is a steady temperature rise upto 65°C for continuous sonication. Upto 35°C temperature was recorded at 1.5 min beyond which there is a steady temperature rise upto 45°C for pulse sonication. Higher temperatures in continuous sonication are obtained as there is no time for relaxation of fluid layers unlike pulse sonication. Optimal yield of 98% and 93.5% were obtained for 20 mL sample during pulse and continuous sonication respectively. Optimal yield of 96.8% was achieved during pulse sonication for 50 mL reactor and thereafter yield started decreasing with increase in reactor size. However, large reactor size leads to lower temperatures and hence yield improves with increasing reactor size during continuous sonication.

Bastante et al., 2015, investigated castor oil methyl esters production by conventional mechanical stirring and non convention sonicated transesterification. Various process parameters for biodiesel production under optimal conditions, maximum FAME yield and energy efficiency in terms of Specific Energy consumption (SEC) and Energy Use Index (EUI) were evaluated and compared for both processes. Optimal reaction conditions with conventional mechanical stirrer (operated at 1100 rpm) were: 9/1 M:O molar ratio, 1.5 wt% catalyst concenteration, 50^0C reaction temperature and 180 min reaction time with a maximum biodiesel yield of 97.5%. Optimal reaction conditions with conventional mechanical stirrer (operated at 1100 rpm) were: 70% duty cycle, 40 % sonification amplitude, 4.87/1 M:O molar ratio, 1.4% catalyst concenteration and 228 sec reaction time for a COME yield of 86.57 %. SEC, LCV and EUI with ultrasonic assisted transesterification are 3.41 g/kWh, 30563 J/g and 38.99 respectively as compared to those provided by conventional mechanically agitated transesterification (0.12 g/kWh, 29,717 J/g and 1.02 respectively).

Bokhari et al.[2016] investigated with transesterification of Rubber seed oil into its methyl esters at inlet pressure varying from 1-3.5 bar for varying plate geometries in 50 L pilot hydrodynamic cavitation reactor. Optimal biodiesel production conditions were obtained when the reaction mixture passes through orifice plate with 21 holes (1mm diameter each) and the pressure at inlet to orifice plate is 3 bar. Process parameters were optimized using Response Surface Methodology (RSM) and the values obtained were M:O molar ratio 6:1, 1 wt % catalyst concenteration, reaction temperature 55°C and reaction time 18 min. Reaction time reduced by 5 times and energy efficiency increased 6.5 folds when biodiesel is produced in hydrodynamic cavitation reactor in comparision to mechanical stirrer.

Choudhury et al., 2014, investigated ultrasound-assisted transesterification of raw Jatropha curcas oil using heterogeneous solid catalyzed (CaO) in a two stage process of esterification and trans-esterification. The formation of active catalyst $Ca(OMe)_2$ is confirmed through XRD and process parameters for biodiesel production were optimized using analysis a statistical experimental design. The optimum conditions for maximum biodiesel yield are: M:O molar ratio 11, catalyst loading of 5.5 wt.% and reaction temperature approximately equal to 64°C. The activation energy for transesterification is found to be 133.5 kJ/mol. The use of heterogeneous catalyst increased activation energy by 4 times as compared to the use of homogeneous alkali catalyst. Ultrasonic assisted severe micro-circulation improved mass transfer characteristics which lead to decrease in activation energy by nearly 20%, in comparision with mechanically stirred reactors.

Moholkar et al., 2000, investigated the acoustic pressure field and the spatial distribution of the cavitation phenomena in a dual frequency ultrasonic reactor. Numerical simulations were used for optimizing the process parameters in a dual frequency acoustic field. It is investigated that proper adjustment of variables such as frequency ratio and the pressure amplitude ratio of the two acoustic waves and the phase difference between the two waves is used to manage the mode (stable or transient) and spatial distribution of the cavitation events. Two chief disadvantages, directional sensitivity and surface erosion can be surmounted by use of dual frequency acoustic field.

Zhang et al., 2015, investigated the optimization of biodiesel production from microalgae by direct transesterification while using co-solvents. The maximum biodiesel conversion is 90.02 ± 0.55 wt.% for the following optimal parameters: n-hexane to 75% ethanol volume ratio of 1:2, reaction temperature 90 °C, reaction time 2.0 h, mixed solvent dosage 6.0 mL and catalyst volume 0.6 mL.

Zhou et al., 2016, investigated and compared biodiesel production in straight tube, coil and fixed bed reactor with fixed bed reactor having a shortest stable time of 30 min. Maximum biodiesel yield of 80.11% for the following optimal values of process parameters: M:O molar ratio 42:1, reaction time 150 min and reaction temperature 300 °C.

A continuous process of biodiesel production using supercritical extraction and non-catalytic supercritical methanol transesterification was established.

Nishimura et al., 2003 examined biodiesel production from vegetable oil using low frequency ultrasonic (28-40 kHz) assisted biodiesel reactor. A very high yield of approximately 98% was achieved at a frequency of 28 kHz while a substantial decrease in reaction time was achieved using a 40 kHz ultrasonic frequency.

Colucci et al., 2005, investigated the increased mass transfer and kinetic rate associated with increased interfacial area and activity and micro-circulation when low frequency ultrasonic waves (20 kHz) were applied to heterogeneous mixture of reactants. Application of ultrasonic irradiation lead to reduction of processing time to less than 30 s and the separation time to less than 60 min.

Hielscher et al., 2011, investigated the effect of ultrasonic irradiation on reaction variables such as catalyst concenteration, M:O molar ratio and reaction time on biodiesel yield. Furthermore, ultrasonic irradiation in Hielscher Reactor demonstrated very low energy requirements (very high energy efficiency), when compared to mechanically agitated stirring and hydrodynamic cavitation reactor.

Kawashima et al., 2009, investigated the biodiesel production using supercritical methanol, ethanol, propanol and butanol. Rapid reaction rate with yield upto 95% for first 10 mins of reaction time was obtained with a temperature range of 250-400 ^{o}C . Requirement of high alcohol to oil molar ratio was observed.

Kusiana et al., 2001, investigated biodiesel production from vegetable oil using supercritical methanol in the absence of catalyst. The presence of water in the transesterification reaction did not have any effect on reaction rate and biodiesel yield. Moreover, the presence of definite quantity of water increased the formation of methyl esters and esterification of FFA together in one step process. Rapeseed oil was converted into its methyl esters in 4 min only. However, temperature and pressure as high as 250–400 ^{o}C and 35-60 MPa respectively were necessary for methanol to reach supercritical state.

Demirbas, 2008, investigated the use of tetrahydrofuran (THF) as a co-solvent with methanol. After complete transesterification, clear separation biodiesel-glycerol phases were obtained and both the excess alcohol and co-solvent were recovered easily in a one step process.

2.3 Optimization of Reaction Parameters

Betiku et al., 2014, investigated the conversion of high FFA yellow oleander oil (YOO) into biodiesel in a two step esterification and transesterification process. Pretreatment or the esterification process was optimized using RSM whereas both RSM and Artificial Neural Network (ANN) were used to optimize conversion of pre-treated oil into biodiesel. The optimal conditions for pretreatment (using RSM) are: M:O ratio 0.35 (v/v), H_2SO_4 amount 0.78% (v/v), reaction time 60 min and reaction temperature 55°C. The optimal conditions for transesterification (using RSM) are: M:O ratio 0.3 (v/v), calcinated plantain peels (CPP) amount 3.0% (w/v) and reaction time of 90 mins with methyl ester yield of 95.25%. The optimal conditions for transesterification (using ANN) are: M:O ratio 0.3 (v/v), calcinated plantain peels (CPP) amount 3.0% (w/v) and reaction time of 75 mins with methyl ester yield of 94.97%. This yield was validated with an experimental value of 95.05% (w/w). ANN was analysed to be more effective and accurate optimization technique because of its higher R2 value and comparatively lower ADD value wrt to RSM.

Sinha et al., 2008, investigated biodiesel production from rice bran oil (RBO). Optimal conditions for production of RBO methyl esters (RBOME) were obtained as: 55°C reaction temperature, 60 mins reaction time, 9/1 M:O molar ratio and 0.75% NaOH catalyst concenteration (w/w). RBOME characterization analysis lead to a conclusion that properties of RBOME obtained under optimal conditions were almost similar to that of petrodiesel, and it is recommended to be used in unmodified CI engines.

Patle et al., 2014, investigated two step biodiesel production of high FFA waste cooking palm oil. Both the steps were simulated considering fatty acid composition of palm oil and in depth kinetics, in Aspen Plus simulator. Quantitative trade-offs among objectives such as economics, heat duty and organic waste facilitates for superior decisions regarding the process design for production of waste cooking palm oil alkyl esters.

Rahimi et al., 2014, investigated soybean oil methyl ester production with KOH as catalyst, in a micro reactor. Biodiesel production was carried out for a given value of reaction variables in circular tubes with 0.8 mm hydraulic diameter. The process design for biodiesel production used Box–Behnken method for improved results, which were then examined for optimal conditions by RSM. The optimum values of reaction variables for biodiesel production were obtained as: M:O molar ratio of 9/1, catalyst loading 1.2 wt.% and reaction temperature 60°C with biodiesel yield of 89%. For the following optimal conditions, biodiesel yield can be increased upto 98% at reactant residence time of 180 s.

Antolin et al., 2002, investigated optimization of reaction variables for sunflower oil methyl ester production by Taguchi's methodology. Characterisation of sunflower methyl esters were done to test several properties such as viscosity, flash point, CFPP and acid value to analyse its suitability for use in CI engines.

Boulifi et al., 2013, investigated optimization of RBOME production through transesterification using RSM based on two-variable central composition design (CCD). The optimal values of reaction variables, reaction temperature and catalyst loading were found to be 45°C and 0.74% wt for a high biodiesel yield of 99.4%. Oxidative stability of RBOME was analysed for a storage period of 24 months and the acid value, peroxide value, viscosity and iodine value were tested as a function of time.

Rabu et al., 2013, investigated biodiesel production from Waste Cooking Oil (WCO) through different process designs with an aim of obtaining highest yield and purity. Highly pure WCO methyl ester yield of 95% was produced for the optimal conditions of: 12/1 M:O molar ratio, 1% w/w NaOH catalyst concenteration for continuous mechanical agitation of 2 h at 60°C. Chemical kinetics was found for the optimal conditions which followed 1st order reaction rate with a rate constant ranging from 0.0035 to 0.0106 min^{-}1.

Hoda et al., 2010, investigated optimization of CSOME production using NaOH as catalyst. Reaction temperatures below 50°C, never lead to the complete transesterification of CSO for any values of M:O molar ratios and catalyst concenteration for a reaction time of 60 minutes. Reaction temperature of 50 to 60°C was found to be suitable for optimal production of biodiesel as the temperatures above 60°C causes difficulty in washing step. Furthermore, the optimal M:O molar ratio was found to be 6:1

Bojan et al., 2011, investigated transesterification of high FFA Jatropha Curcas Oil and optimized reaction variables using RSM with CCD application. Five-level three factors problem lead to 20 experiments to analyse the effect of varying reaction variables on biodiesel yield. A second-order polynomial regression model was fitted and found adequate with R2 of 0.9879. It was analysed from the model that maximum biodiesel yield would be 81.93% at the following optimal vales of reaction parameters: Reaction temperature of 61°C, catalyst concenteration 2.06% w/w of oil and M:O molar ratio of 7.28:1.

Leduc et al., 2009, investigated Life Cycle Analysis (LCA) and supply chain from biomass harvesting to biodiesel production and final delivery to end consumer. A mixed integer linear programming model is used to find optimal number of plants and their suitable geographic locations. Various scenarios were investigated for yield, biomass cost, cake price, glycerol price, transport cost and investment costs involved with biodiesel production. It was concluded that feedstock cost has the maximum effect on biodiesel cost. Investment cost and the glycerol price were not affected that much.

2.4 Economic and Enviourmental Aspects of Biodiesel

Mosarof et al., 2015, investigated possibility of palm oil as use as substitute to petro-diesel in terms of its performance, environmental effects, wear characteristics, and economic feasibility. Among various edible vegetable oils, palm oil is a comparatively sustainable, eco-friendly and economically feasible. Use of palm oil in CI engines is found to reduce exhaust emissions of HC, CO, CO_2 and smoke, however NO_x emissions increased.

Sajid et al., 2016, investigated and compared environmental effects of biodiesel production from non-edible Jatropha oil and WCO using LCA. It was analysed that crop cultivation of Jatropha has higher environmental impact as compared to WCO. However, transesterification of Jatropha oil was more economical and eco-friendly than biodiesel production from WCO as WCO requires additional use of chemicals and energy for its pretreatment. The total environmental impact is 74% less in case of using WCO as feedstock for biodiesel production as compared to non-edible Jatropha oil.

Pereira et al., 2016, investigated Global Warming Potential (GWP), Terrestrial Acidification Potential (TAP), Respiratory Inorganic Effects (RIE) Non-Renewable Energy (NRE) consumption. Green House Gases (GHG) emissions and energy savings associated with Jatropha fuel production and operation in a typical LPV in India. LCA of Jatropha fuel showed that it is competitive with petro-diesel in terms of NRE and GHG emissions; however it resulted in higher local environmental impacts (RIE and TAP categories).

2.5 Stability of Biodiesel

Dos et al., 2011, investigated the effect of molecular structure of species involved in the oxidation reactions of unsaturated fatty acid esters at varying temperatures. Among all the esters studied, ricinoleate was seen to be the least vulnerable to oxidation at high temperatures.

Xin et al., 2008, investigated the effect of amount of unreacted tocopherol left with change in temperature. Researchers observed that the amount of unreacted tocopherol reduces with the increase of temperature above 300°C.

2.6 Gaps in Literature Review

- Researchers have not yet investigated batch type ultrasonic cavitation for biodiesel production for large sample size, suitable for industrial application.
- Any research work based on closed loop ultrasonic cavitation is not available.
- Research work to reduce the size of cavitation zone for large scale production of biodiesel by ultrasonic cavitation techniques is not available.
- There is a vast scope of research in analysing process parameters such as power output, frequency and amplitude of ultrasonics to optimize biodiesel yield in ultrasonic cavitation reactor.
- The effects of pressure variation on biodiesel yield and transesterification reaction rate in sonochemical reactors has not been carried out so far.
- A number of non-edible oils are yet to be explored for biodiesel production. Considering the limited availability of edible oils, working on newer non edible oils suitable for biodiesel production in developing countries like India is the need of time.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

Implementation of proper research methodology is a major aspect for achieving successful research with proper results and its generalisation. It can be characterized from numerous points of view, for example, methodology, ways, strategies and systems that are connected to fuse and accumulate all applicable data for the exploration.

This chapter deals with defining and formulation of research problems on the basis of exhaustive literature review and shows the approaches of raw material procurement, characterisation of raw Jatropha oil, experimental design, optimization of reaction parameters, property testing, energy analysis and economic analysis of biodiesel production. The list of equipments, their calibration and error estimation is also shown in this chapter. Figure 3.1 presents a flow chart which summarizes the research work.

3.2 Formulation of Research Problem

A lot of research has been carried out for biodiesel production from variety of feedstocks, alcohols and catalyst trough various conventional and non conventional techniques. The non conventional techniques include hydrodynamic cavitation, ultrasonic cavitation, super critical alcohol method and transesterification through microwave irradiation. Non conventional techniques have an advantage of being rapid and higher biodiesel yield. Non-catalytic supercritical methanol and microwave irradiation transesterification were found to have rapid reaction rate and higher yield as compared to biodiesel production from cavitation techniques (Kusdiana et al., 2001; Demirbas, 2003; Demirbas, 2002; Han et al., 2005; Barbosa et al. 2006) However, both these techniques are highly energy intensive that limits their use in commercial production of biodiesel.

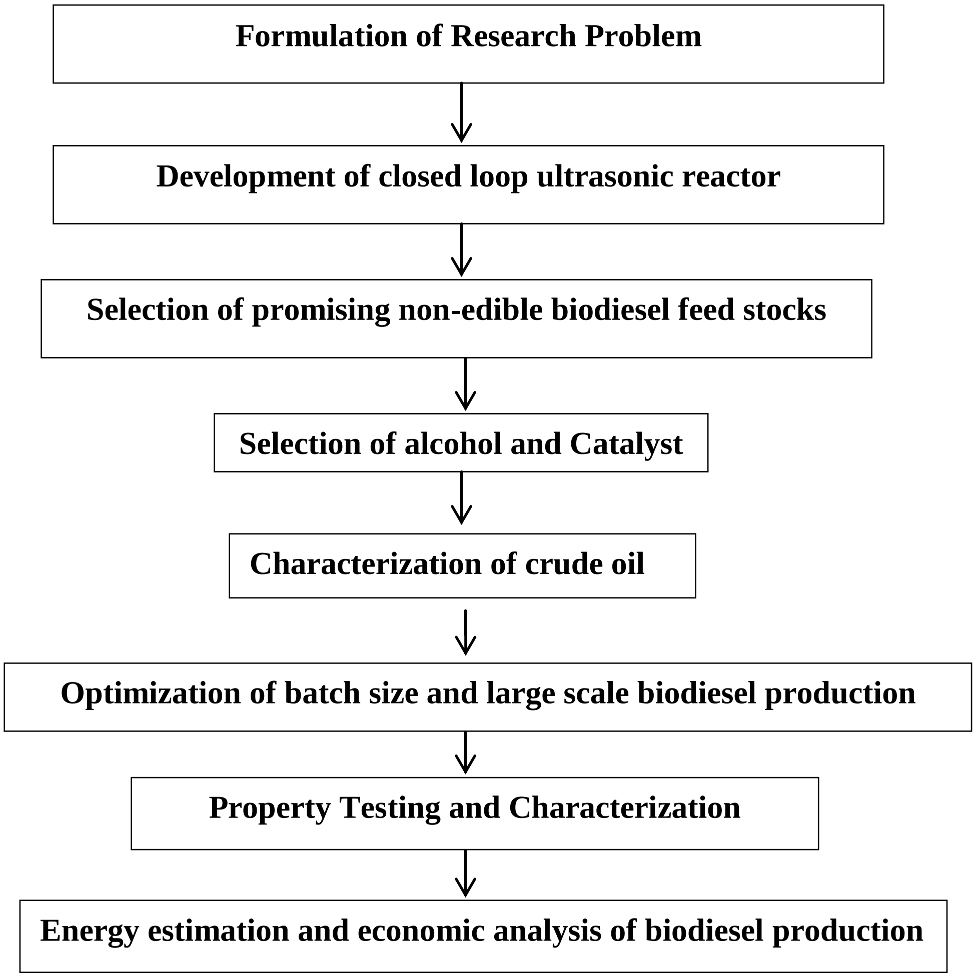


Fig. 3.1: Flow diagram of the research methodology

Hydrodynamic cavitation and ultrasonic cavitation, though a bit slower than other non conventional techniques, are much more energy efficient processes. Among them, ultrasonic cavitation is found to be superior to hydrodynamic cavitation in terms of reaction rate and overall energy consumption. Hence, it was formulated to investigate the effect of ultrasonic irradiation on biodiesel production. Other things on which decision has to be made are: the choice of vegetable oil, alcohol and catalyst for biodiesel production. Looking at the potential and interest of Government of India, non edible Jatropha Curcas oil was chosen for experimental investigation. Jatropha Curcas is a poisonous, flowering shrub reaching upto a height of 6m, belonging to spurge family and mostly cultivated in tropical and subtropical regions of the world including Indian Sub Continent. The plant can grow in wastelands and on almost any terrain, even on gravelly, sandy and saline soils with seed production of around 3.5-5 tonnes/ht in 2-3 years time (Wikipedia). Each fruit of Jatropha bears 2-3 seeds and each seed weighs between 600-700 mg (Kandpal et al., 1995). 30-40% oil yield is obtained from Jatropha seeds whereas 45-50% oil yield is obtained from kernels of the seed (Kandpal et al., 1995). Anhydrous methanol (99.8% min.) and NaOH (85% min.) were used as alcohol and homogeneous catalyst respectively for transesterification.

A lot of research has been carried out on optimization of reaction variables and energy requirement estimations in small scale laboratory size, ultrasonic assisted biodiesel production. However, most of the study has been focussed on single frequency ultrasonic reactors. The current research work compares the optimal conditions of reaction variables, biodiesel yield and energy efficiency for horn type, bath type, double frequency and triple frequency flow ultrasonic reactors for laboratory scale biodiesel production.

Further, a combined process closed loop reactor (including mechanical stirrer, hydrodynamic cavitation and sonochemical reactor) was developed in order to make a reliable and efficient system for large scale industrial production of biodiesel. Optimization of reaction variables and energy requirement estimations were carried out for the closed loop reactor. Last, but not the least, biodiesel production was investigated for a closed loop ultrasonic reactor under pressurized conditions.

Table 3.1: Property testing equipments and test methods

Properties	Measurement Apparatus	Test Method
Density at 15°C (g/cc)	Stabinger Viscometer-SVM 3000 (Anton Paar India Pvt. Ltd.)	ASTM D1298
Viscosity at 40^0C (cSt)	Stabinger Viscometer-SVM 3000 (Anton Paar India Pvt. Ltd.)	ASTM D7042/D445
Flash point & Fire point (^{0}C)	Pensky-Martens closed cup apparatus (Normalab, France)	ASTM D 92
Pour point and Cloud	Pour point and Cloud and tester -automatic NTE 450 (Normalab, France)	ASTM D 2500 and D 97
CFPP (^{0}C)	Automatic NTL 450 (Normalab, France)	ASTM D 6371
Calorific value(MJ/kg)	Parr 6100 calorimeter (IKA, UK)	ASTM D240
Oxidation Stability (h)	873 Rancimat (Metrohm, Switzerland)	EN 14112

3.3 Equipments and Test Methods

The characterisation and property testing of the raw Jatropha Curcas oil and their respective methyl esters were done using ASTM D 6751 standard. Table 3.1 shows the description of equipments and test methods for characterization.

3.4 Determination of Acid Value

An initially measured quantity of refined Jatropha Curcas oil was taken into a beaker with subsequent addition of 50 ml of Iso-propanol. The iso-propanol and refined oil mixture was heated upto 50-55°C to ensure proper dilution of oil in 2-Propanol. Phenolphthalein (2-3 drops) was added as colour indicator in the titration process. The titration process was then started by gradually adding the base titrant (NaOH solution) of known normality. The volume of titrant used for complete titration is the measure of the acid value of the crude oil. Acid value is a measure of FFA content present in oil.

$$AV = \frac{MW \times N \times V}{W} \tag{3.1}$$

where,

MW =Molecular weight of NaOH.

N= Normality of NaOH solution (0.1 N).

V= Volume of NaOH solution.

W = Weight of oil sample.

3.5 Fatty acid composition determination

Fatty acid composition of seed oil was analyzed by gas chromatography and found to be in accordance with results shown in Table 3.2.

Table 3.2: Fatty acid composition of Jatropha seed oil (Foidl et al., 1996; Akintayo, 2004; Sarin et al., 2007)

Type of fatty acid	Carbon number	Acid name	% Composition
Saturated	C8:0	Caprylic	-
	C10:0	Capric	0.0-0.10
	C12:0	Lauric	-
	C14:0	Myristic	0.0-1.40
	C16:0	Palmitic	13.0-19.50
	C18:0	Stearic	6.80-9.70
	C20:0	Arachidic	0.0-0.40
Monounsaturated	C16:1	Palmitoleic	0.80-1.40
	C18:1	Oleic	34.30-53.0
Polyunsaturated	C18:2	Linoleic	20.0-43.20
	C18:3	Linolenic	0.0-3.0

3.6 Design of Combined Process Closed Loop Reactor

The schematic diagram of the combined process reactor (CPR) is shown in Figure 3.2. The set-up consists of a closed loop circuit comprising a feed tank connected with mechanical stirrer (250 rpm operated by 180 W motor), reciprocating pump (max 600 **psi**, 3 **hp**, 950

rpm and 36 LPM capacity) and ultrasonic reactor. Two Pizzo electric transducers, both operating at 30 kHz frequency and maximum power rating of 400 W are installed on opposite sides of ultrasonic reactor which enables effective penetration of ultrasonic waves in the reaction mixture. Continuous intermixing of the liquid takes place inside the feed tank with the help of mechanical stirrer. The suction side of the pump is connected to the bottom of the feed tank. The liquid from pump is then discharged to the sonochemical reactor where ultrasonic cavitation process takes place. The liquid in the main line after undergoing the cavitation process is supplied to the feed tank where mechanical stirring of the rest of the liquid is going on. The liquid again goes to the reciprocating pump and continuous circulation of liquid takes place in a closed loop circuit. Thus the bulk portion of the liquid undergoes mixing via mechanical stirrer and rest of the fluid is undergoing ultrasonic cavitation at any given instant of time. This increases the reliability of system as the biodiesel production continues even if one component of the system fails. A coupling accommodating orifice plate can be inserted in the main passage line in order to have simultaneous hydrodynamic cavitation as well.

3.7 Energy Estimations

To determine and compare the energy cost of biodiesel produced from different techniques, a parameter is defined to show the mass of biodiesel as a function of energy consumption for its synthesis. The parameter called Specific Energy Consumption (SEC) is used to determine energy cost per kg of biodiesel produced as shown in Eq. (3.2).

$$\text{SEC} = \frac{\text{Energy Consumed}}{\text{Mass of biodiesel syntheseised}} = \frac{\text{Power} \times \text{Time}}{\text{Mass of biodiesel syntheseised}} \left(\frac{\text{kWh}}{\text{kg}}\right) \quad (3.2)$$

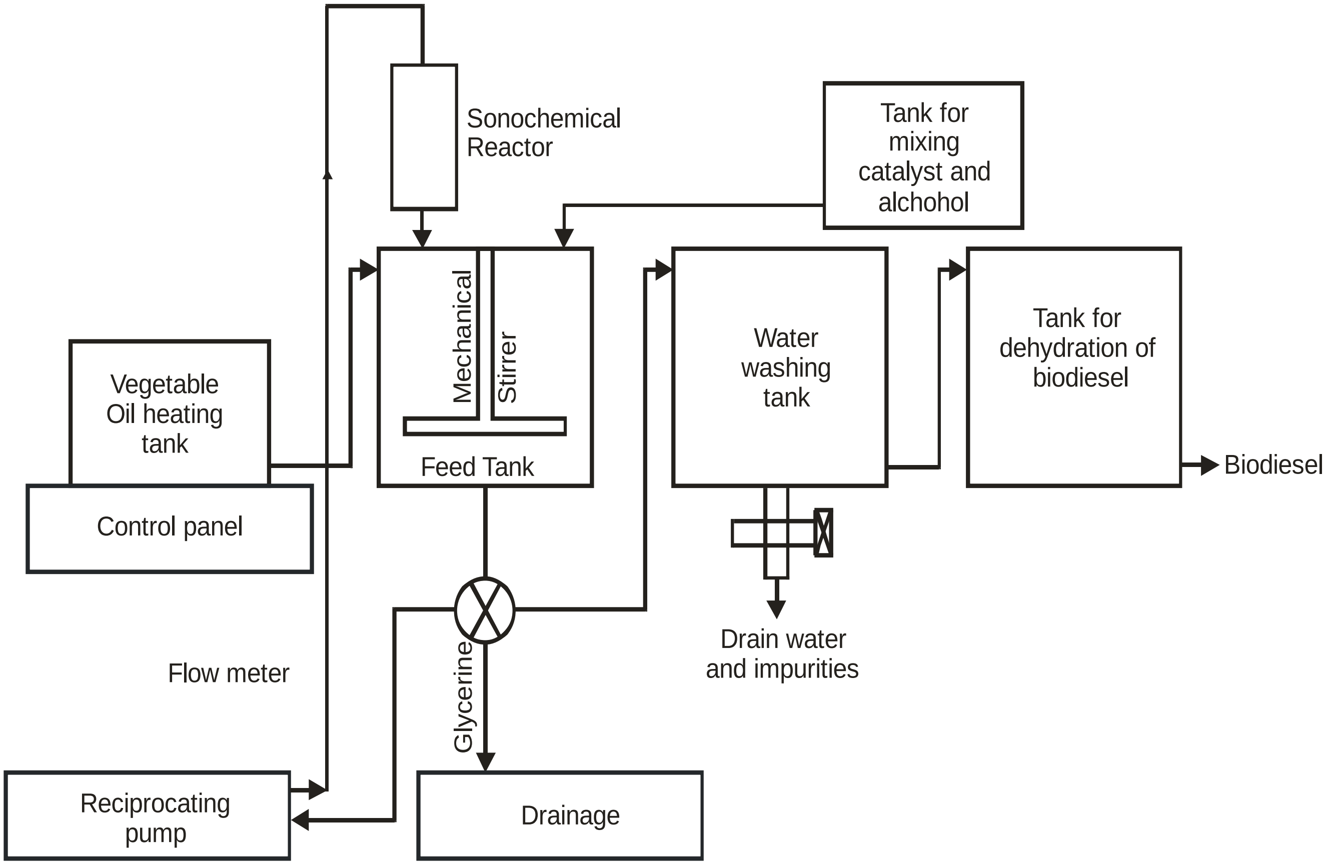


Fig. 3.2: Schematic diagram of combined process reactor

Biofuels are termed as renewable sources of energy. However, these sources of energy are not 100 % renewable because synthesis of biofuels required consumption of energy that might be obtained from non-renewable energy resources. It should be noted that energy generated from the biofuels must be significantly higher than that consumed for its synthesis. Another interesting parameter to estimate the worth of biofuel produced is the Energy Use Index (EUI) that reflects the ratio between the amounts of energy generated by combustion of fuel to the amount of energy consumed in its synthesis (Eq. (3.3)).

$$\text{EUI}=\frac{\text{Lower Caloific Value}\left(\text{J/g}\right)}{\text{Amount of energy per mass required for its synthesis (J/g)}} \quad (3.3)$$

3.8 Biodiesel Production

A two-step transesterification process (acid catalyzed esterification followed by alkaline catalyzed transesterification) is employed to produce biodiesel. In the first step, high FFA JCO is esrterified using H_2SO_4 catalyst. The free fatty acids react with methanol to produce methyl esters and water. The pre-treated JCO is then heated up to 110-120°C and kept at this temperature for about 5-7 minutes in order to remove water content of oil and prevent soap formation. It is then allowed to cool upto 60°C. An appropriate quantity of methanol and NaOH were mixed and stirred until entire sodium hydroxide dissolves in methanol. Suitable number of biodiesel samples at appropriate time intervals was obtained. After completing the process, the sample was poured into a separation flask for 4-5 hour for the separation. Methyl esters were separated from glycerol employing gravity separation and were finally water washed to remove soap and residual catalyst to obtain pure biodiesel.

3.9 Calibration

The value of an unknown parameter is obtained through measurement. This measured value may or may not be the actual or true value. If the measured value is very close to the true or actual value, then it is a very accurate measuring system. Therefore, accuracy in the readings of the measuring instruments should be maintained by frequently comparing and adjusting with the readings of another standard instrument. This process is called calibration. Before taking the readings, all the experimental equipments were calibrated and test results were repeated three times and readings were found to be repeatable.

3.10 Error Estimation

In any experiment, errors and uncertainties may arise from instrument selection, condition, environment, calibration, reading and test planning. All experiments may have some errors irrespective of the care which is exerted. Uncertainty analysis is required to prove the accuracy of the experiments. Final results in any experiment are obtained from the primary measurements.

Table 3.3: Uncertainty in measuring various parameters

Parameter	Range	Uncertainty	Accuracy
Voltage	0-260 V	± 0.5 V	upto 0.5% of reading
Weight	0-600 g	± 0.005 g	upto 0.3% of reading
Calorific Value	0-40,000 J/g	± 2J/g	upto 0.3% of reading
Viscosity	0.3 – 10000 mPa.s	± 0.05 mPa.s	upto 0.5% of reading
Density	0 - 3 g/cm^3	± 0.0005 g/cm^3	0.0001 g/cm^3
Pressure	0-50 bar gauge pressure	± 0.5 bar	upto 0.25% of reading
Temperature	10 – 150^{o}C	± 0.1 ^{o}C	upto 0.3% of reading

CHAPTER 4

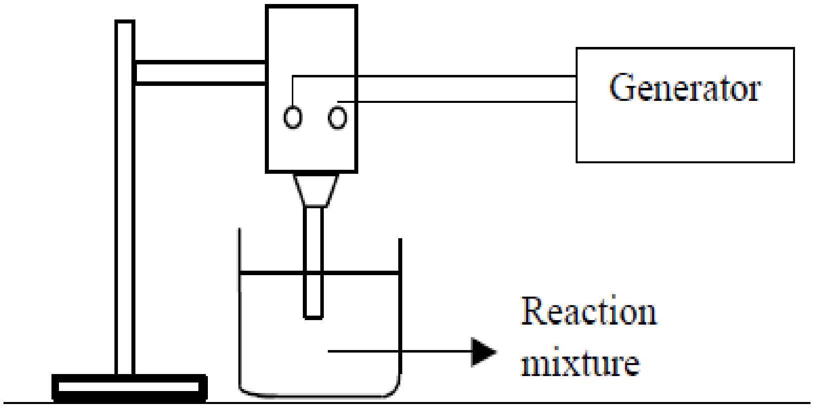
OPTIMIZATION OF SMALL SCALE BIODIESEL PRODUCTION THROUGH ULTRASONIC CAVITATION

4.1 Working principle of Ultrasonic Cavitation

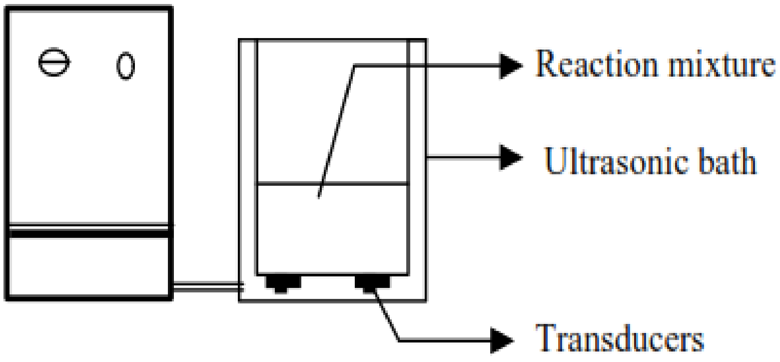
Biodiesel is produced using a non-classical form of energy where the low-frequency ultrasonic wave causes cavitation in the reaction mixture. Cavities are formed in the fluid by the irradiation of power ultrasonic with sufficient energy in immiscible liquid (oil and alcohol are immiscible with each other). Cavitation results in the formation of fine micro bubbles at various places of the reactor. Turbulence caused by collapsing of these bubbles disrupts the phase boundary between two immiscible liquids leading to emulsification of the mixture to yield biodiesel through the transesterification reaction. Energy liberation of the order of 1 to 10^{18} kW/m^3 during ultrasonic cavitation process, raise the overall temperature of reaction mixture upto a level required to carry out transesterification reaction without using external heating agency (Gogate et al., 2005).

4.2 Experimental Set Up

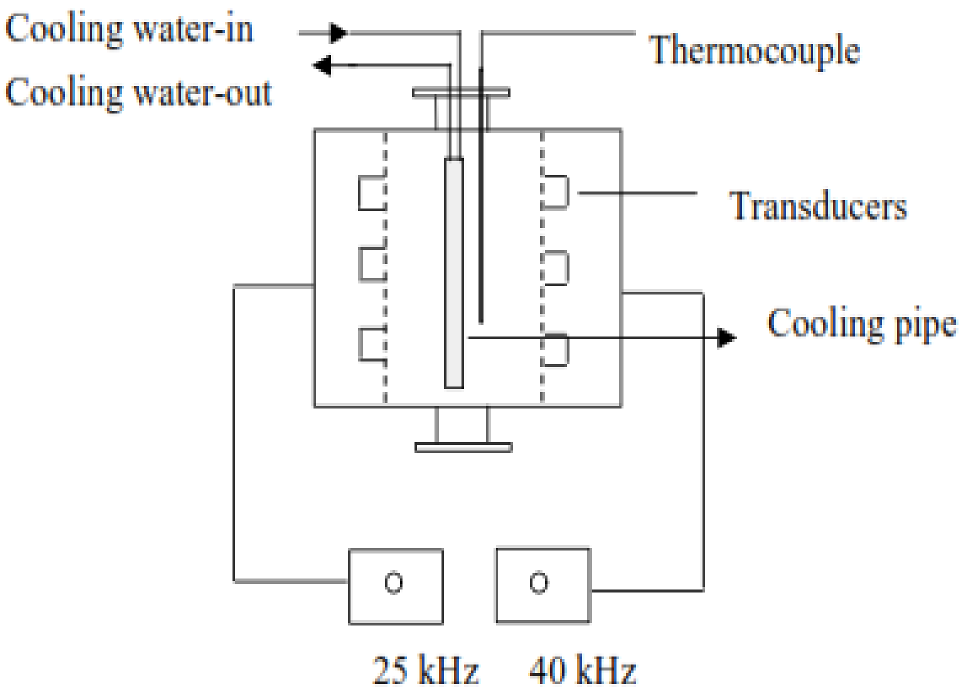
Figure 4.1 (a) shows 150 Watt (W) ultrasonic horn type biodiesel reactor with an ultrasonic frequency of 28 kHz. The horn type ultrasonic reactor is suitable for preparing biodiesel samples of 50 to 300 gram. In the present experiment, the reactor has been utilized for 200-gram sample. Figure 1(b) shows an ultrasonic bath reactor having a fixed operating frequency of 22.7 kHz, a rated power dissipation of 150 W and maximum operating capacity of 3 kg. Three transducers are placed at the bottom of the reactor in a triangular fashion. In the present study, the reactor has been utilized for 2 kg sample. Figure 1(c) shows a double frequency flow cell ultrasonic reactor having a vessel with a maximum capacity to hold 2.5 kg sample. It consists of two set of transducers (each set having three transducers placed longitudinally) mounted on the vessel surface in a diametrically opposite manner. One set of transducers is operating at 28 kHz and another set at 40 kHz with equal power ratings of 120 W per set of transducers. In the present study, the reactor has been utilized for 1.5 kg sample. Figure 1(d) shows a triple frequency hexagonal flow cell ultrasonic reactor having a vessel with a maximum capacity to hold 5 kg sample. It consists of six set of transducers (each set having three transducers placed longitudinally) mounted on six faces of the hexagon. Two set of transducers on opposite faces of hexagon have similar irradiating frequency. Transducers have operating frequency of 22, 28 and 40 kHz with equal power ratings of 120 W per set of transducers. In the present study, the reactor has been utilized for 3.5 kg sample.



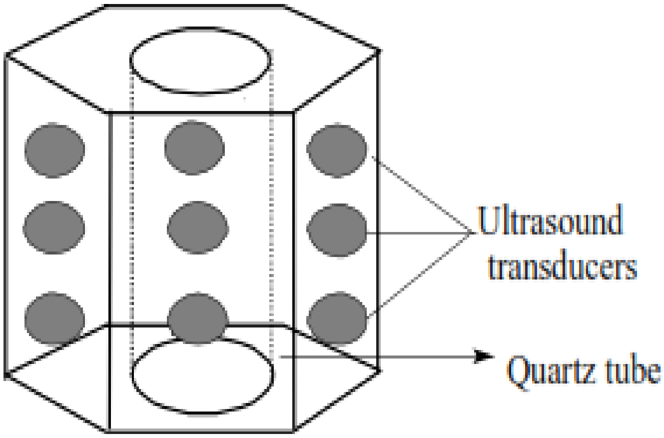
(a) Schematic diagram of ultrasonic horn



(b) Schematic diagram of ultrasonic bath reactor



(c) Schematic diagram of double frequency flow cell ultrasonic reactor



(d) Schematic diagram of triple frequency hexagonal flow cell ultrasonic reactor

Fig. 4.1: Various types of ultrasonic reactors

4.3 Biodiesel Production

The acid value of raw JCO obtained was 9.1. However, the acid value after acid catalysed esterification reduced to 1.7. Alkali catalysed transesterification is recommended only if the Acid value is reduced to less than 2 (Veljkovic et al., 2012). Experiments were carried out for a molar ratio of 9:1 and 1% NaOH concentration. Table 4.1 represents the amount of raw materials used in different reactors. An appropriate quantity of methanol and NaOH were mixed and stirred until entire sodium hydroxide dissolves in methanol. This liquid mixture was then mixed with JCO (after undergoing pre-treatment, heating at 110-120^{O}C (for water removal) and then cooling to 60 ^{O}C) in the vessel of ultrasonic reactors. Biodiesel yields were calculated for sufficient number of samples at appropriate time intervals. After completing the process of ultrasonic cavitation, the sample was poured into a separation flask for 4-5 hour for the separation. Methyl esters were separated from glycerol employing gravity separation and were finally water washed to remove soap and residual catalyst to obtain pure biodiesel.

Table 4.1: Amount of oil, methanol and catalyst for conventional and ultrasonic reactors

Reactor	JCO (kg)	Molar Ratio	Methanol (kg)	Catalyst (%)	Catalyst (kg)
Mechanical Stirring	0.2	9:1	0.0331	1	0.002
Horn	0.2	9: 1	0.0331	1	0.002
Bath	2	9: 1	0.3312	1	0.02
Double Frequency	1.5	9: 1	0.2484	1	0.015
Triple Frequency	3.5	9: 1	0.5796	1	0.035

4.4 Results and Discussion

Jatropha oil methyl ester yield as a function of time, for various types of ultrasonic reactors and mechanical stirrer is analyzed for the following reaction parameters: methanol to oil molar ratio of 9:1, NaOH catalyst concentration 1% w/w of oil, reaction temperature 60^{O}C and operating ultrasonic power equal to 50-80% of the rated maximum power.

Figure 4.2 shows the variation of jatropha oil methyl ester yield when all the ultrasonic reactors are operated at 50% of their rated maximum power. Optimal yield of biodiesel achieved is: 8.1 % in 300 mins reaction time for mechanical stirrer, 93.5% in 70 minutes reaction time for a horn type ultrasonic reactor, 94.1% in 60 minutes for bath-type ultrasonic reactor, 95.5% in 50 minutes for a double frequency flow cell ultrasonic reactor and 95.4% in 30 minutes for triple frequency flow cell ultrasonic reactor as shown in Table 4.2.

Figure 4.3 shows the variation of jatropha oil methyl ester yield when all the ultrasonic reactors are operated at 60% of their rated maximum power. Optimal yield of biodiesel achieved is: 94% in 60 minutes reaction time for a horn type ultrasonic reactor, 94.1% in 50 minutes for bath-type ultrasonic reactor, 95.2% in 40 minutes for a double frequency flow cell ultrasonic reactor and 95.4% in 20 minutes for triple frequency flow cell ultrasonic reactor as shown in Table 4.3.

Figure 4.4 shows the variation of jatropha oil methyl ester yield when all the ultrasonic reactors are operated at 70% of their rated maximum power. Optimal yield of biodiesel achieved is: 94.5% in 60 minutes reaction time for a horn type ultrasonic reactor, 94.4% in 50 minutes for bath-type ultrasonic reactor, 95.5% in 40 minutes for a double frequency flow cell ultrasonic reactor and 96% in 20 minutes for triple frequency flow cell ultrasonic reactor as shown in Table 4.4.

Figure 4.5 shows the variation of jatropha oil methyl ester yield when all the ultrasonic reactors are operated at 80% of their rated maximum power. Optimal yield of biodiesel achieved is: 93.5% in 60 minutes reaction time for a horn type ultrasonic reactor, 93.7% in 50 minutes for bath-type ultrasonic reactor, 94.5% in 40 minutes for a double frequency flow cell ultrasonic reactor and 95.5% in 20 minutes for triple frequency flow cell ultrasonic reactor as shown in Table 4.5.

Table 4.2: Optimal yield at 50% of rated maximum power

Process	**Optimum Yield (%)**	**Reaction time (mins) corresponding to optimum yield (%)**
Mechanical Stirring	80.1	300
Horn	93.5	70
Bath	94.1	60
Double Frequency	95.5	50
Triple frequency	95.4	30

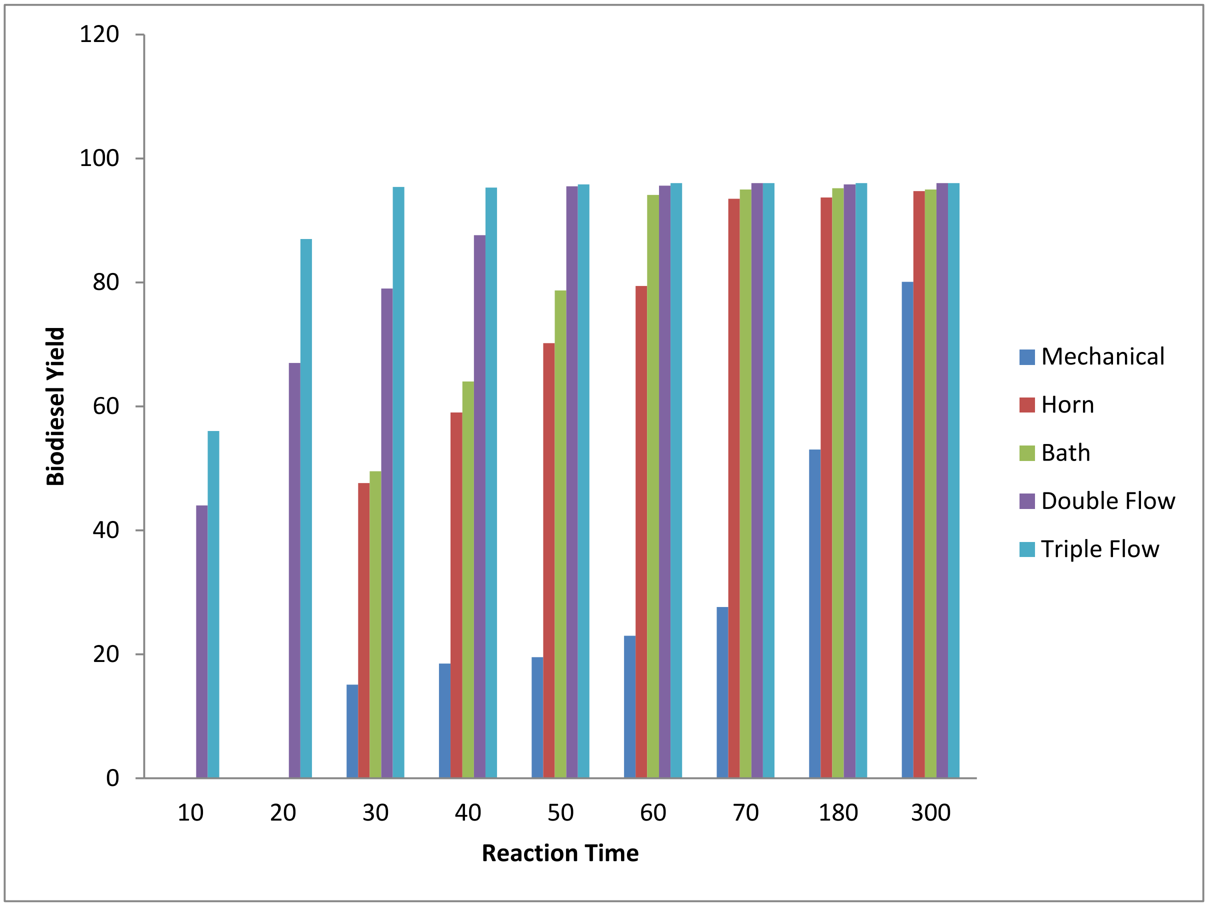


Fig. 4.2: Biodiesel yield when ultrasonic reactor is operated at 50% of rated power

Table 4.3: Optimal yield at 60% of rated maximum power

Process	**Optimum Yield (%)**	**Reaction time corresponding to optimum yield (%)**
Mechanical Stirring	80.1	300
Horn	94	60
Bath	94.1	50
Double Frequency	95.2	40
Triple frequency	95.4	20

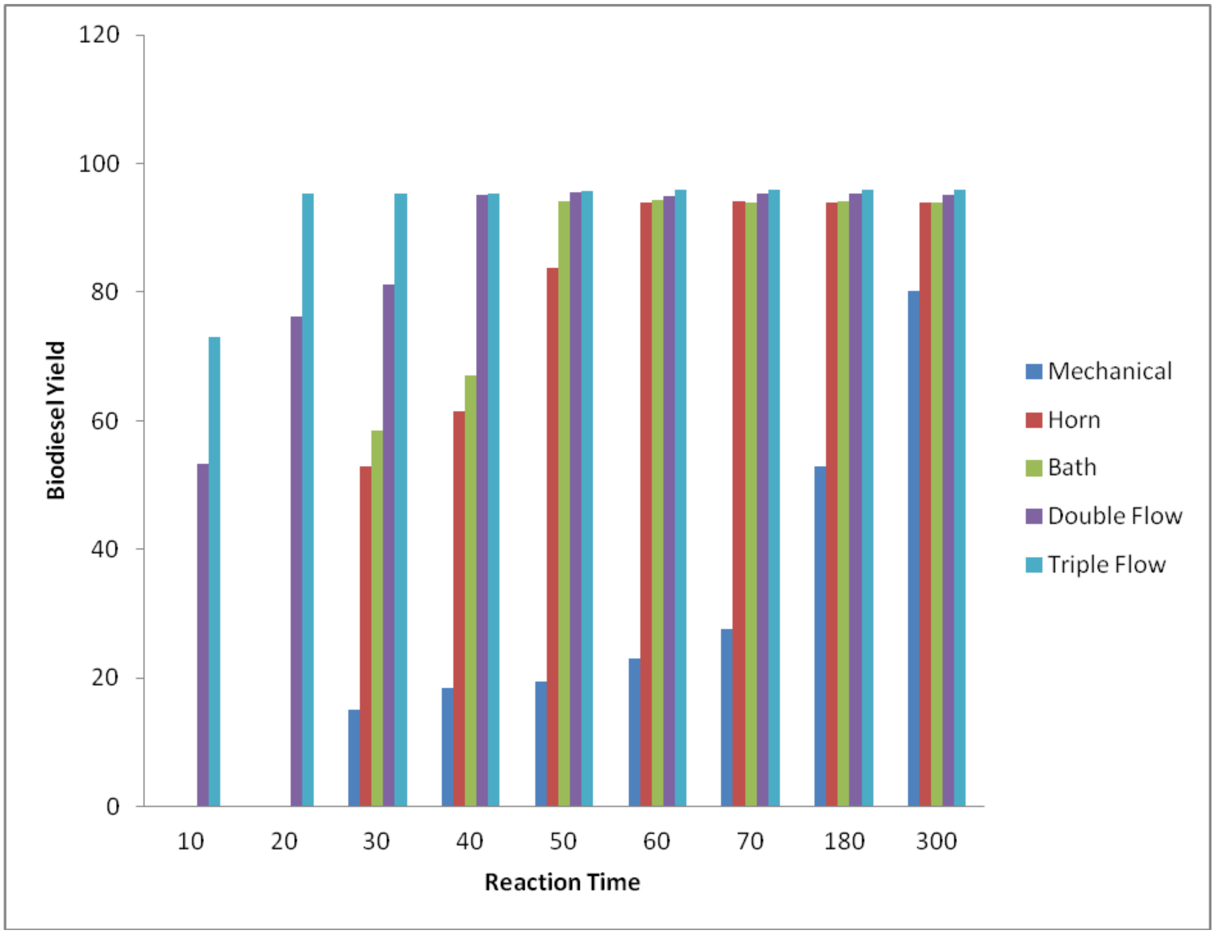


Fig. 4.3: Biodiesel yield when ultrasonic reactor is operated at 60% of rated power

Table 4.4: Optimal yield at 70% of rated maximum power

Process	**Optimum Yield (%)**	**Reaction time corresponding to optimum yield (%)**
Mechanical Stirring	80.1	300
Horn	94.5	60
Bath	94.4	50
Double Frequency	95.5	40
Triple frequency	96	20

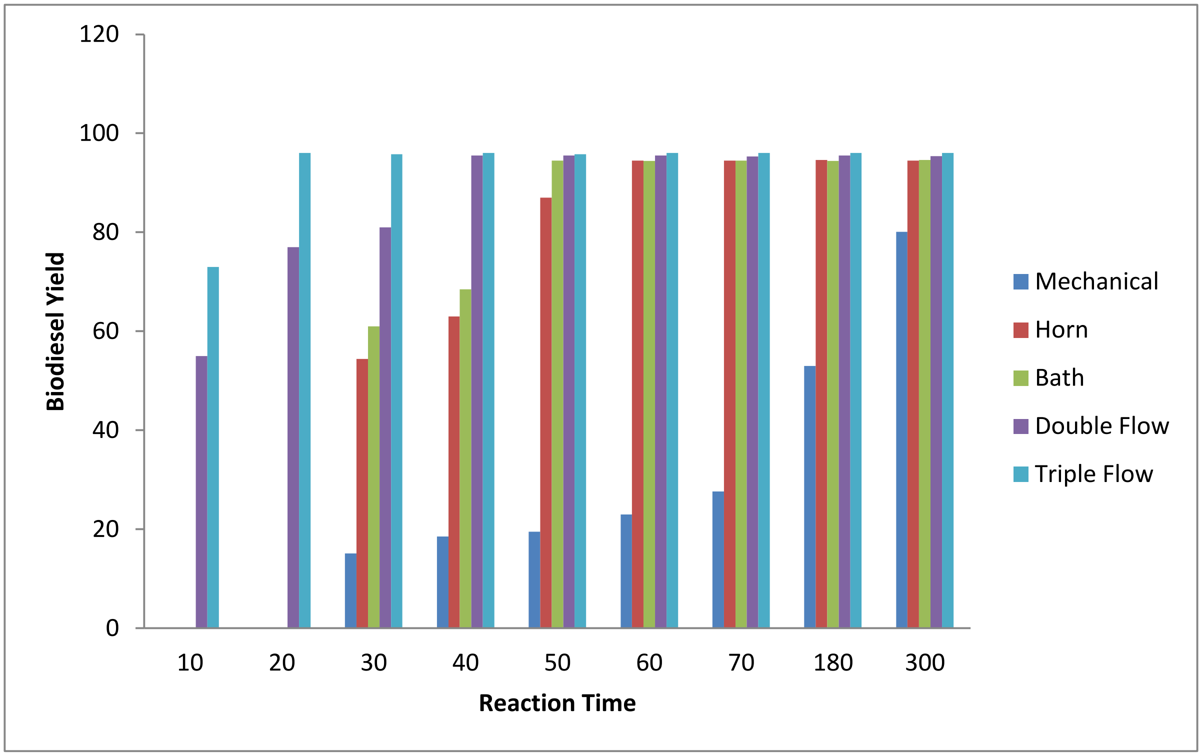


Fig. 4.4: Biodiesel yield when ultrasonic reactor is operated at 70% of rated power

Table 4.5: Optimal yield at 80% of rated maximum power

Process	**Optimum Yield (%)**	**Reaction time corresponding to optimum yield (%)**
Mechanical Stirring	80.1	300
Horn	93.5	60
Bath	93.7	50
Double Frequency	94.5	40
Triple frequency	95.5	20

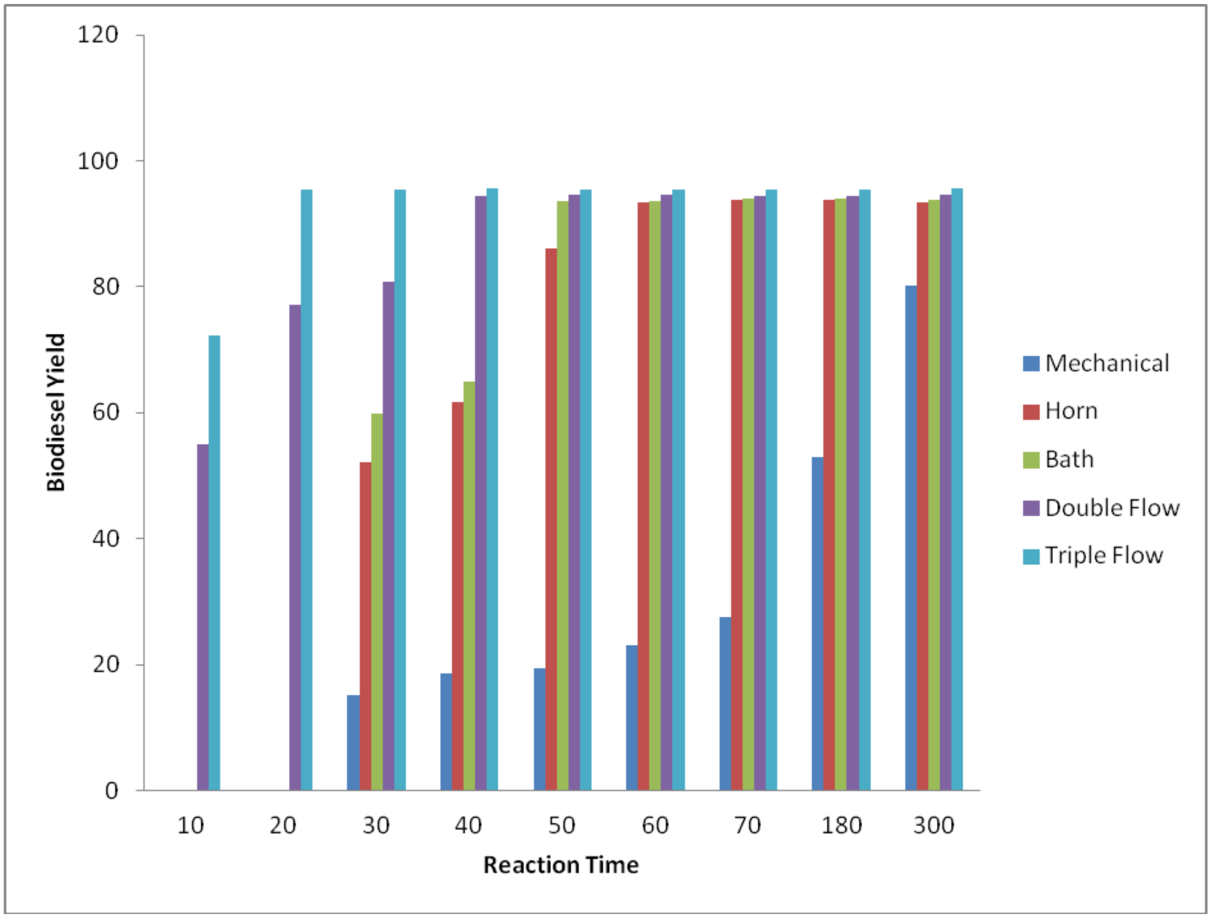


Fig 4.5: Biodiesel yield when ultrasonic reactor is operated at 80% of rated power

From the above experiments, it can be analyzed that time required for completion of reaction decreases with increasing power and attains a minimum reaction time for 60-70% range of the maximum rated power for all types of ultrasonic reactor. At higher ultrasonic power, cavitation bubbles starts combining to form larger and stable bubbles which lead to poor penetration of ultrasonic energy in the reaction mixture and ineffective mixing of immiscible reactants. Similar trend of variation of biodiesel yield with ultrasonic power is reported by Baddy (Baddy et al., 2013), Kumar (Kumar et al., 2010) and Stavarache (Stavarache et al., 2005). Ji (Ji et al., 2006) also investigated production of soybean oil methyl esters under ultrasonic irradiation conditions by working on three levels of power conditions [100 W, 150 W and 200 W] and found that 150 W power gave the optimal results.

The order of reaction time irrespective of the ultrasonic power is: Triple frequency flow cell < Double frequency flow cell < Bath type < Horn type ultrasonic reactor. Rapid reaction rate with triple frequency flow cell ultrasonic reactor is probably due to its effective utilization of energy dissipated into the system for cavity formations. Uniform energy dissipation along with efficient energy utilization maximizes energy and mass transfer in the immiscible reaction mixture through ultrasonic reactors with multiple transducers. Horn type reactors have the least reaction rates due to the formation of concentrated cavitation zone and reduced cavitation intensity in the reaction mixture lying outside the cavitation zone.

4.5 Energy Estimation

Energy consumed in production of biodiesel in an ultrasonic reactor involves:

1. Energy required for heating the raw oil upto 110-120°C to remove the moisture content of oil.
2. Energy for maintaining the temperature of reaction mixture at 55-65°C.
3. Power provided to the ultrasonic transducers.

Energy required to remove the moisture content of raw oil and to maintain the reaction mixture at 55-65°C is insignificantly small in comparison to overall energy consumption of the biodiesel production process. Hence, these energies are neglected while calculating SEC and EUI of biodiesel produced. Table 4.6 shows the analysis and comparison of energy consumption in four different ultrasonic reactors at optimal conditions of biodiesel production. Triple frequency flow cell ultrasonic reactor is investigated to be the best reactor for energy consumption and economic worth for biodiesel synthesis due to its minimum SEC (0.043 kWh/kg) and maximum EUI (243.54.70) respectively. Triple frequency flow cell ultrasonic reactors have additional advantages of rapid reaction rate which makes it most suitable ultrasonic reactor for biodiesel synthesis. Double frequency flow cell can also be considered as a highly energy efficient reactor for biodiesel synthesis because of its low SEC of 0.065 kWh/kg and high EUI of 162.1.

Table 4.6: Analysis of Specific Energy Consumption and Energy Unit Index

Reactor	Biodiesel (kg)	Power (W)	Time (min)	Energy Consumed (kWh)	SEC (kWh /kg)	LCV (kJ/g)	EUI
Horn	$0.2\times\frac{94}{100}$ $=0.188$	0.6×150 $=90$	60	0.09	0.47	37.8	21.95
Bath	$2\times\frac{94.1}{100}$ $=1.88$	$3\times(0.6\times150)$ $=270$	50	0.225	0.12		87.73
Double frequency	$1.5\times\frac{95.2}{100}$ $=1.482$	$2\times(0.6\times120)$ $=144$	40	0.096	0.065		162.1
Triple frequency	$3.5\times\frac{95.4}{100}$ $=3.34$	$6\times(0.6\times120)$ $=432$	20	0.143	0.043		243.54

4.6 Conclusion

Production of biodiesel from jatropha oil was carried successfully and the following conclusions were obtained from our experimental investigation. Time required for completion of reaction decreases with increasing power and attains a minimum reaction time for 60-70% range of the maximum rated power for all types of ultrasonic reactor. Optimum biodiesel yield for horn, bath, double frequency and triple frequency ultrasonic reactors are 94% in 60 minutes, 94.1% in 50 minutes, 95.2 % in 40 minutes and 95.4 % in 20 minutes respectively at 60% of the maximum rated power conditions. Triple frequency flow cell is found to be the most energy efficient ultrasonic reactor for biodiesel. SEC and EUI for triple frequency flow cell ultrasonic reactor are 0.043 KWh/kg and 243.54 respectively.

CHAPTER 5

OPTIMIZATION OF BIODIESEL PRODUCTION IN A COMBINED CLOSED LOOP REACTOR

5.1 Objective of the Present Research Work

Although many studies have focused on mechanical stirring and ultrasonic biodiesel production for variety of feedstock, no substantial work was found using combined process to enhance the reliability and energy efficiency of biodiesel production system. In this work a process reactor has been made for the combined mechanical stirring and ultrasonic cavitation processes. It is designed to enhance the reliability of the system, so that both the process can be simultaneously used to make the biodiesel. The reactor is capable of processing the biodiesel from 5-100 kg of oil.

5.2 Biodiesel Production

An appropriate quantity of methanol and NaOH were mixed and stirred until entire sodium hydroxide dissolves in methanol. This liquid mixture was then mixed with JCO (after undergoing pre-treatment, heating at 110-120^{O}C (for water removal) and then cooling to 60 ^{O}C) in the feed tank of the reactor and the reactor is switched on. Suitable numbers of sample of 100 ml each were collected from the bottom of the feed tank at appropriate time interval.

Experiments were carried out for methanol to oil molar ratio of 4.5/1, 6/1 and 9/1 and catalyst concentration of 0.5, 0.75, 1 and 1.5 %w/w oil. Table 5.1 shows amount of raw materials used for biodiesel production. The biodiesel yield was also recorded for 70% of maximum rated ultrasonic irradiation power conditions. Optimal parameters (catalyst concentration, molar ratio and reaction time) were obtained for biodiesel production in combined process reactor and the results were compared with value of optimal parameters obtained for biodiesel production using mechanical stirrer and ultrasonic reactor independently. Ultrasonic reactor is switched off and the control valve is closed, (the reaction mixture is not allowed to pass through ultrasonic reactor) when biodiesel production is carried out using mechanical stirrer independently. The motor operating the mechanical stirrer (MS) is switched off and control valve is opened when biodiesel production is carried out using ultrasonic reactor (UR) independently.

5.3 Results and Discussions

5.3.1 Mechanical Stirring

1 mole of triglyceride is reacted with 3 moles of alcohol to yield biodiesel and glycerine in a transesterification reaction. However, the reversible nature of the reaction requires use of excess alcohol in order to shift the reaction toward product side. It has been reported in the literature that optimal molar ratio and catalyst concentration are 9:1 and 1.5% respectively for transesterification of Jatropha Curcas oils by mechanical stirring technique. Fig. 5.1 shows methyl ester yield at varying reaction time (50-350 mins) at a fixed interval of 50 mins. A general trend of increase in biodiesel yield with reaction time is observed with maximum yield of 79.2% obtained for 300 min sample. Thereafter, the biodiesel yield is held constant and shows minimal variation with increase in reaction time.

Table 5.1: Amount of oil, alcohol and catalyst used

Molar Ratio	**Catalyst (w/w oil)**	**Jatropha oil (kg)**	**Methanol (kg)**	**Catalyst (kg)**
4.5:1	0.5	5	0.828	0.025
	0.75	5	0.828	0.0375
	1	5	0.828	0.5
	1.5	5	0.828	0.75
6:1	0.5	5	1.104	0.025
	0.75	5	1.104	0.0375
	1	5	1.104	0.5
	1.5	5	1.104	0.75
9:1	0.5	5	1.656	0.025
	0.75	5	1.656	0.0375
	1	5	1.656	0.5
	1.5	5	1.656	0.75

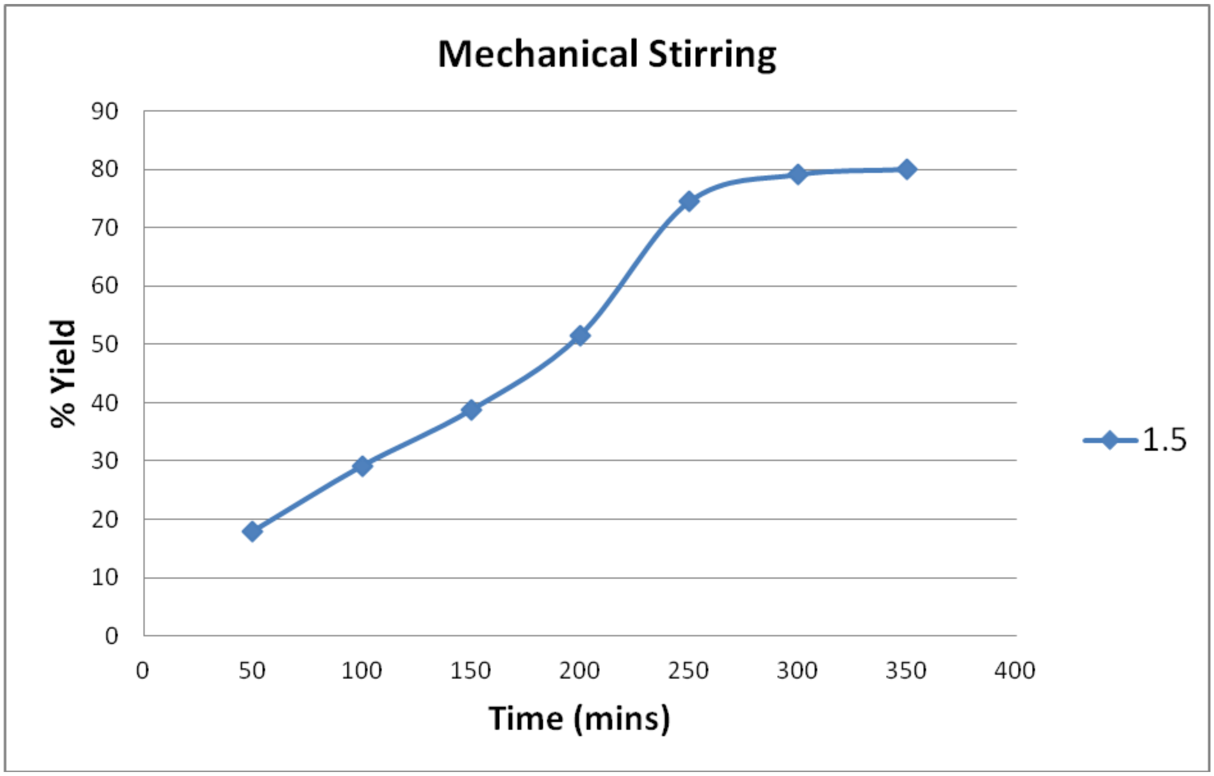
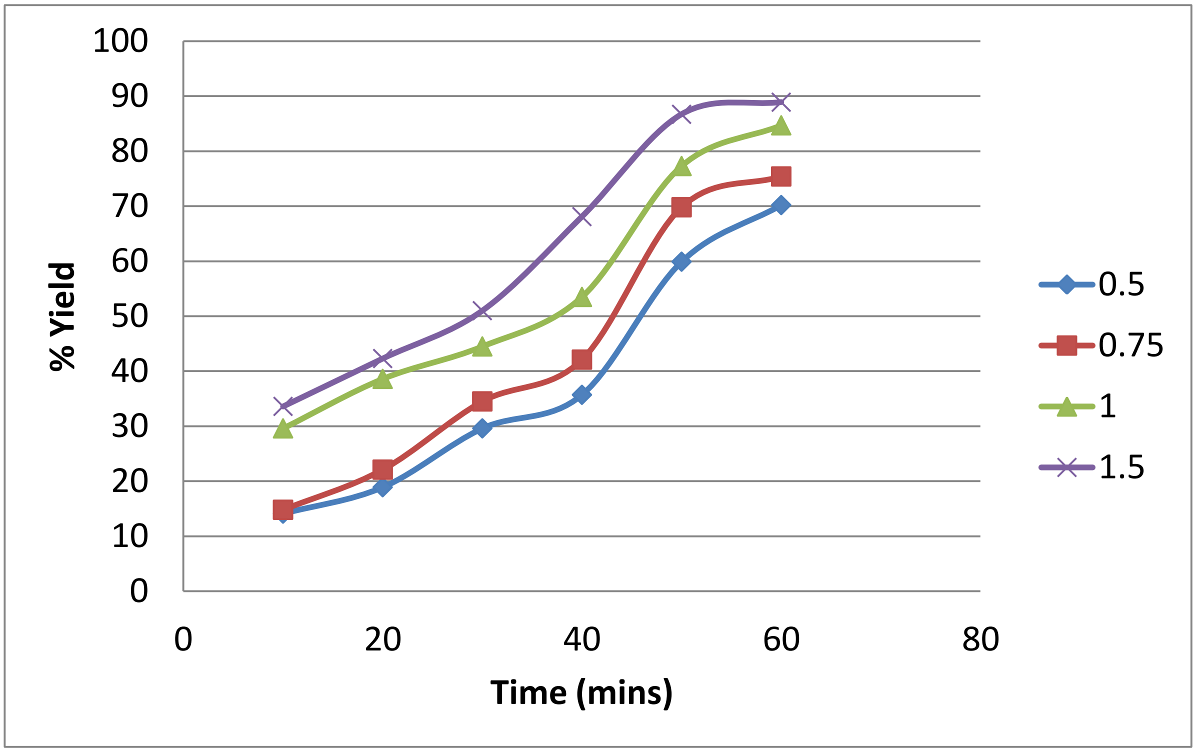


Fig. 5.1: Biodiesel yield for molar ratio 9:1 and 1.5% catalyst under mechanical stirring conditions

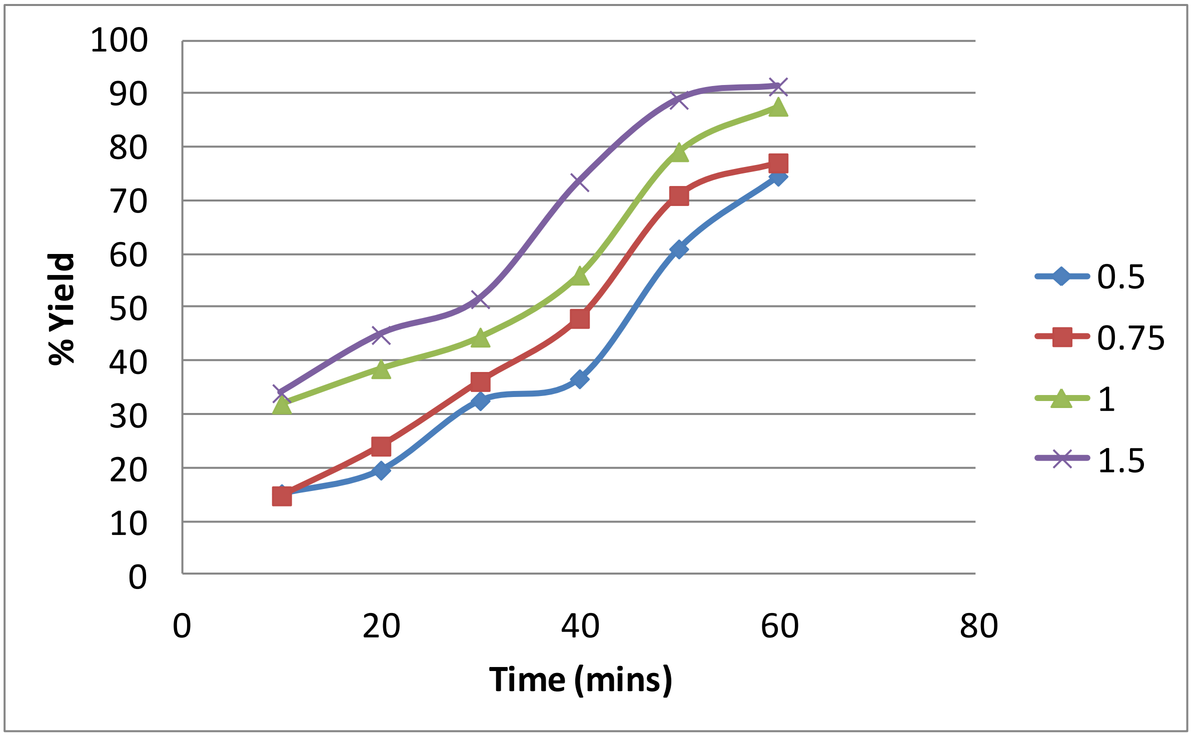
5.3.2 Closed Loop Ultrasonic Reactor

Figure 5.2 (a), (b) and (c) shows biodiesel yield at varying reaction time (10-60 mins) under ultrasonic irradiation conditions at different catalyst concentrations (0.5, 0.75, 1 and 1.5% by w/w oil) for molar ratio 4.5:1, 6:1 and 9:1 respectively. Many researchers have investigated the effect of ultrasonic power on reaction time and reaction yield. Baddy et al. [31] came to the conclusion that maximum biodiesel yield of 91% for Jatropha oil was obtained for 60% of the maximum ultrasonic power irradiation conditions. Initially, biodiesel yield increases with increase in ultrasonic power, then attains an optimum value at some intermediate value of ultrasonic power and finally shows an inverse trend with further increase in ultrasonic power. Similar trend of variation with ultrasonic power is reported by Kumar et al. [32] and Stavarache et al. [33]. Based on the literature, 70% ultrasonic power was selected as a central value to obtain optimal process parameters for biodiesel production. A general trend of increase in biodiesel yield with reaction time is observed with increasing catalyst concentration and molar ratio. Many researchers have investigated that increasing the catalyst concentration and molar ratio beyond their optimal values leads to slight decrease in biodiesel yield due to difficulty in extraction of biodiesel from the product mixture. Optimal biodiesel yield of 94% is obtained for 60 min reaction time, 9/1 molar ratio and 1% catalyst concentration.

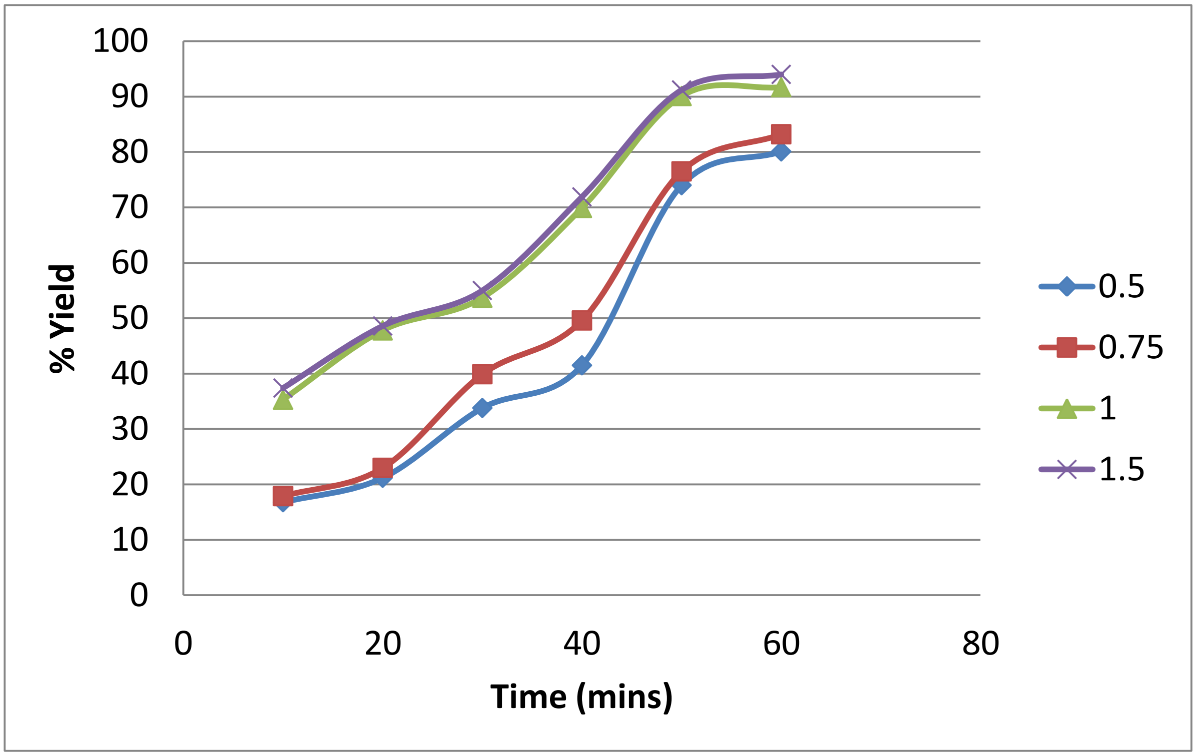
Figure 5.3 (a), (b) and (c) shows methyl ester yield at varying reaction time (10-60 mins) in a combined process reactor at different catalyst concentrations (0.5, 0.75, 1 and 1.5 % by w/w oil) for molar ratio 4.5:1, 6:1 and 9:1 respectively. Optimal biodiesel yield of 96.5% is obtained for 50 min reaction time, 6/1 molar ratio and 1% catalyst concentration at 70% of maximum ultrasonic power irradiation. It is also analysed that requirement of excess methanol (methanol more than the stoichiometric requirement of transesterification reaction) is less in combined process reactor as compared to biodiesel production in mechanical stirring conditions and ultrasonic reactor (molar ratio is 9:1 in both cases).



(a) Biodiesel Yield at Molar Ratio 4.5:1 at different catalyst concenteration

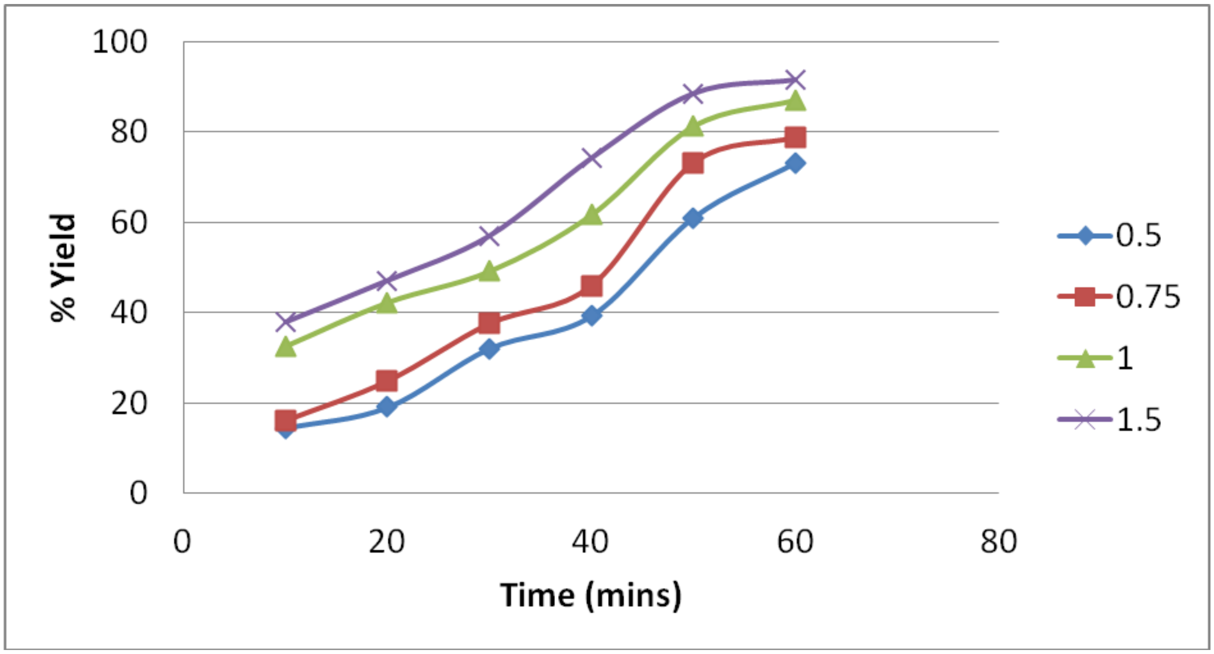


(b) Biodiesel Yield at Molar Ratio 6:1 at different catalyst concenteration

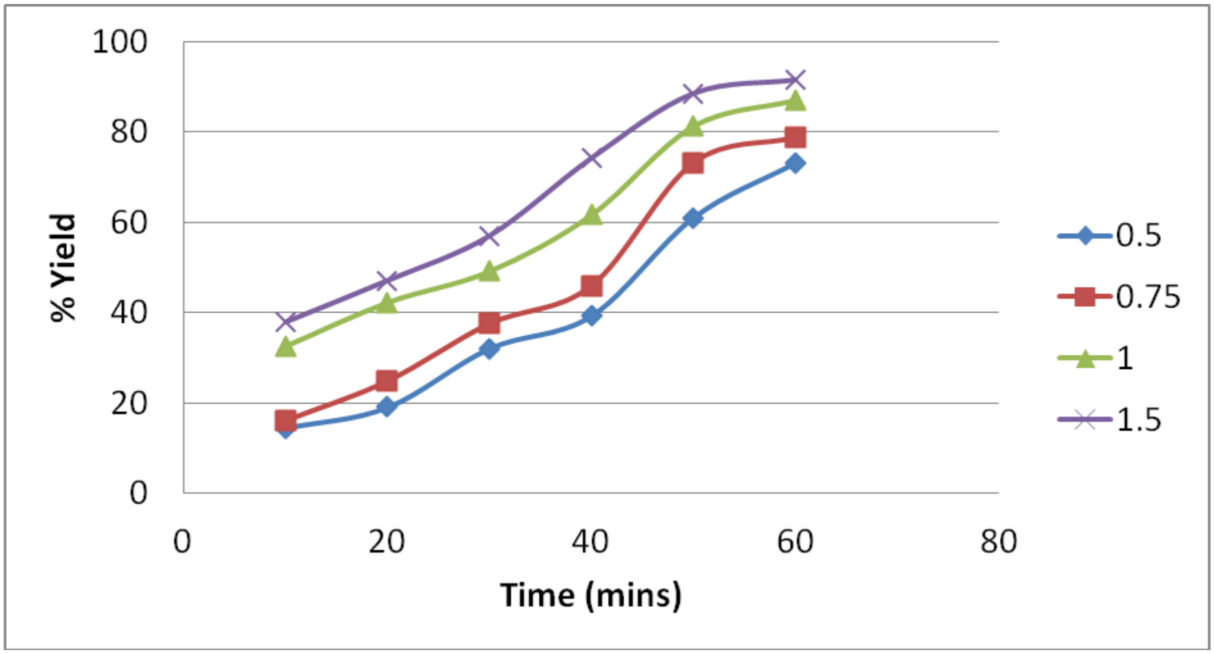


(b) Biodiesel Yield at Molar Ratio 9:1 at different catalyst concenteration

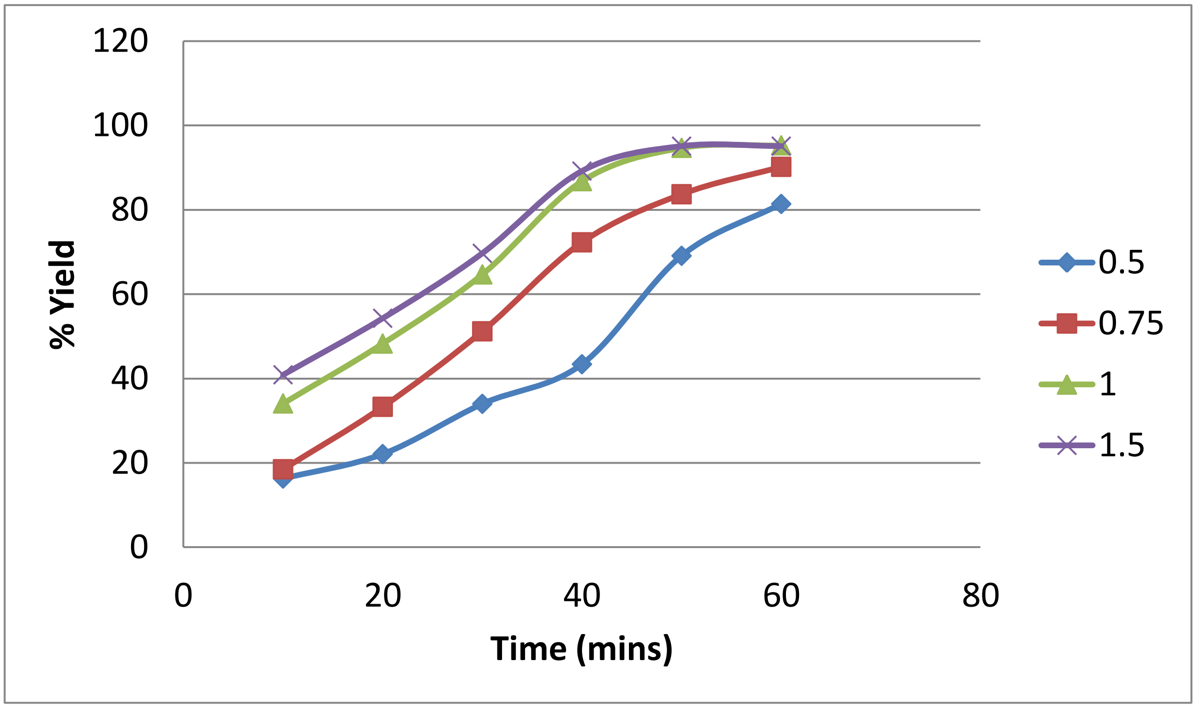
Fig. 5.2: Biodiesel Yield in closed loop ultrasonic reactor



(a) Biodiesel Yield at Molar Ratio 4.5:1 at different catalyst concenteration



(b) Biodiesel Yield at Molar Ratio 6:1 at different catalyst concenteration



(c) Biodiesel Yield at Molar Ratio 9:1 at different catalyst concenteration

Fig. 5.3: Biodiesel Yield in closed loop combined process reactor

5.4 Energy Estimate

Energy consumed in production of biodiesel via mechanical stirrer involves:

1. Energy required for heating the raw oil upto 110-120°C to remove the moisture content of oil.
2. Energy for maintaining the temperature of reaction mixture at 55-65°C.
3. Energy for stirring the reaction mixture.

Energy consumed in production of biodiesel via ultrasonic reactor involves:

1. Energy required for heating the raw oil upto 110-120°C to remove the moisture content of oil.
2. Energy consumed by the reciprocating pump to maintain the flow in closed loop circuit.
3. Power provided to the ultrasonic transducers.

Energy consumed in production of biodiesel via combined process reactor involves:

1. Energy required for heating the raw oil upto 110-120°C to remove the moisture content of oil.
2. Energy consumed by the reciprocating pump to maintain the flow in closed loop circuit.
3. Energy for stirring the reaction mixture.
4. Power provided to the ultrasonic transducers.

Energy required to remove the moisture content of raw oil, maintain the reaction mixture at 55-65°C (in mechanical stirring) and maintain the flow in closed loop circuit (in ultrasonic reactor and combined process reactor) are insignificantly small in comparison to overall energy consumption of the biodiesel production process. Hence these energies are neglected while calculating specific energy consumption of biodiesel production. Table 5.2 shows the analysis and comparison of energy consumption for three different reactors at optimal conditions of biodiesel production. Combined process reactor is investigated to be the optimal process for biodiesel production with respect to cost of energy for biodiesel synthesis due to its minimum SEC (0.213 kWh/kg). However, CPR has additional advantages of lower reaction time, lower requirement of catalyst, and lower requirement of alcohol to oil molar ratio.

Table 5.2: Analysis of Specific Energy Consumption

Reactor	**Mass of Biodiesel (kg)**	**Mechanical Stirrer Power (W)**	**Transducer Power (W)**	**Pump Power (W)**	**Total Power consumed (W)**	**Time (min)**	**Energy Consumed (kWh)**	**SEC (kWh/kg)**
Mechanical Stirrer	$\frac{79.2}{100}\times 5 = 3.96$	180		456	645	300	3.225	0.814
Ultrasonic Reactor	$\frac{94}{100}\times 5 = 4.7$		$0.7\times 2\times 40$ $= 560$	465	1025	60	1.025	0.218
CPR	$\frac{94.2}{100}\times 5 = 4.71$	180	$0.7\times 2\times 40$ $= 560$	465	1205	50	0.39	0.213

5.5 Conclusions

Optimization and energy analysis of biodiesel production from jatropha oil in various types of reactors is carried out successfully and the following conclusions are drawn from the experimental investigations. The optimum reaction conditions with mechanical stirrer are: 300 mins reaction time, 9:1 molar ratio, 1% catalyst with a maximum yield of 79.2%. Optimal biodiesel yield of 94% is obtained for 60 min reaction time, 9/1 molar ratio and 1% catalyst concentration for closed loop ultrasonic reactor. Optimal biodiesel yield of 96.5% is obtained for 50 min reaction time, 6/1 molar ratio and 1% catalyst concentration at 70% of maximum ultrasonic power irradiation. It is also analysed that requirement of excess methanol (methanol more than the stoichiometric requirement of transesterification reaction) is less in combined process reactor as compared to biodiesel production in mechanical stirring conditions and ultrasonic reactor (molar ratio is 9:1 in both cases). SEC for mechanical stirrer, ultrasonic reactor and CPR are 0.814, 0.218 and 0.213 kWh/kg respectively. CPR is found to be most economically viable reactor for biodiesel synthesis.

CHAPTER – 6

PRESSURISED ULTRASONIC PRODUCTION OF BIODIESEL IN A CLOSED LOOP REACTOR

6.1 Objective of the Present Research Work

This research work is based on the development of pressurized ultrasonic test rig and optimization of reaction parameters such as molar ratio, catalyst concentration and pressure for biodiesel production. Although many studies have focused on optimization of biodiesel production from Jatropha curcas oil through conventional stirring and cavitation techniques, no literature is found on the effect of ultrasonic irradiation in a reaction mixture under pressurized conditions. Comparison of optimal reaction variables and energy efficiency for transesterification via pressurized ultrasonic irradiation and unpressurized ultrasonic irradiation in a closed loop system is investigated for the first time.

6.2 Biodiesel Production

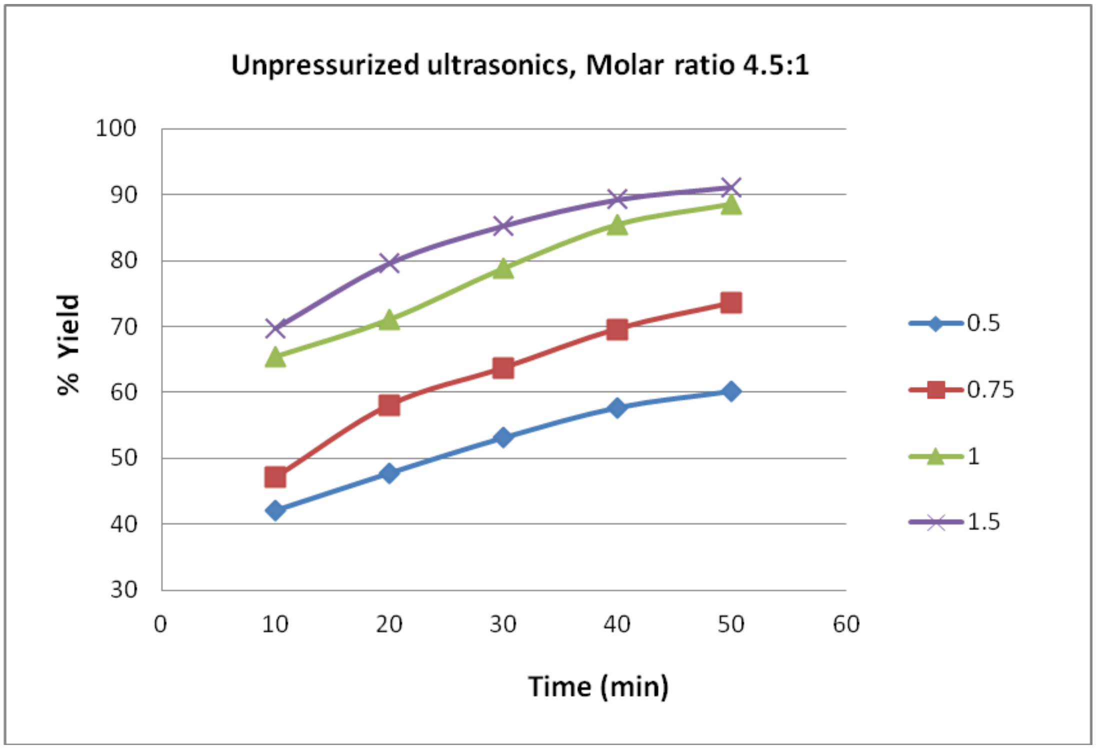
An appropriate quantity of methanol and NaOH were mixed and stirred until entire sodium hydroxide dissolves in methanol. This liquid mixture was then mixed with JCO (after undergoing pre-treatment, heating at 110-120^{O}C (for water removal) and then cooling to 60 ^{O}C) in the feed tank of the reactor. Table 6.1 presents the details of the ingredients used for biodiesel production. Experiments were carried out for molar ratio 4.5/1, 6/1 and 9/1 for 0.5%, 1% & 1.5% catalyst concentration by weight of oil. The liquid mixture is mixed with jatropha oil in the feed tank and then undergoes transesterification reaction in pressurized ultrasonic cavitation reactor. The set-up consists of a closed loop circuit comprising a feed tank (5-100 kg capacity), reciprocating pump (max 600 P.S.I, 3HP, 950 RPM and 36 LPM capacity), control valve and ultrasonic reactor. Two Pizzo electric transducers, both operating at 30 kHz frequency and maximum power rating of 400 W are installed on opposite sides of the vessel to enable uniform energy dissipation and effective utilization of energy dissipated into the system for cavity formation. Discharge from the pump branches into two lines via control valve, one going to the feed tank and the other (main line) going to the ultrasonic reactor. The relative opening of the control valve allows us to change the pressure in the reaction mixture flowing in the main line. The reaction mixture flowing at high pressure in the main line (after undergoing the cavitation process) is fed back to the feed tank from where it again goes to the reciprocating pump and thus a continuous circulation of liquid takes place in a closed loop circuit. If the valve is operated in such a manner that entire mixture from reciprocating pump is passed through the sonochemical reactor at atmospheric conditions, then we obtain a closed loop, unpressurized ultrasonic test rig. The biodiesel yields (as a function of time) are then compared for pressurized and unpressurized ultrasonic cavitation in a closed loop system.

6.3 Results and Discussion

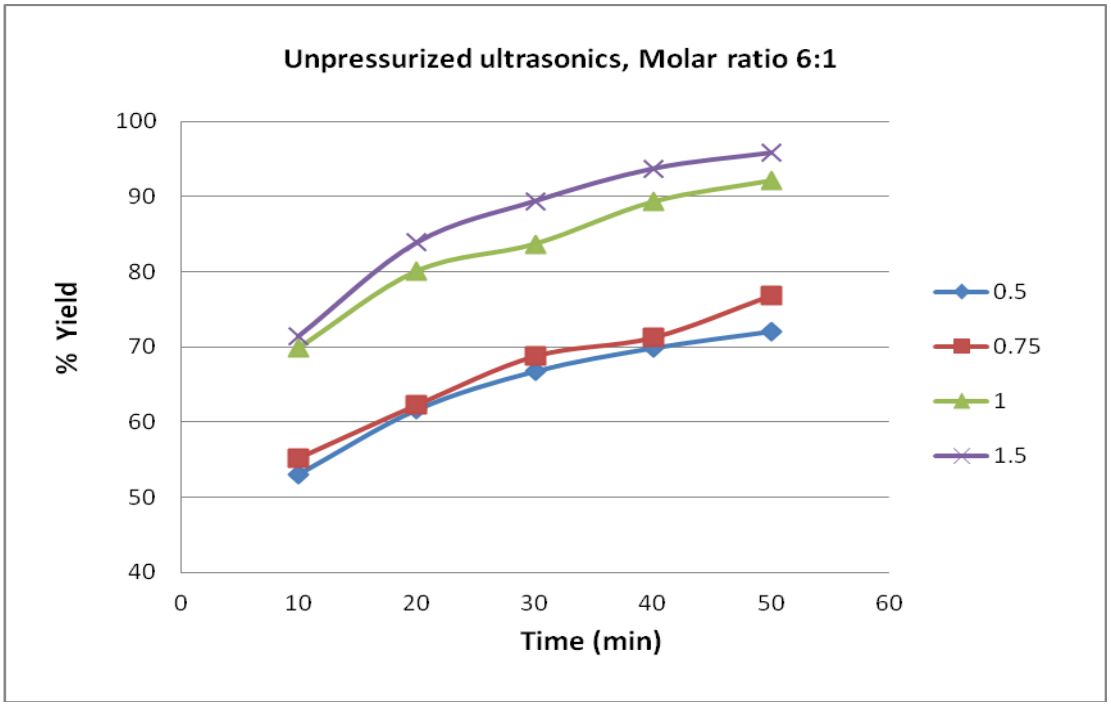
For all the experiments performed, power supply to ultrasonic transducers is maintained at 70% of maximum rated power and the temperature of reaction mixture is controlled between 55°C and 65°C by circulation of water in the jacket of the reactor for a fixed sample size of 5 kg. The general trend of increase in biodiesel yield with reaction time is almost similar for both pressurized and non-pressurized ultrasonic irradiation conditions at all molar ratios and catalyst concentrations. However at high pressures of 15-20 bar, a slight decrease in biodiesel yield is noticed beyond a certain increase in reaction time, catalyst concentration and molar ratio. Figure 6.1 (a), (b) and (c) shows the variation of jatropha oil methyl ester yield as a function of time for unpressurized ultrasonic irradiation conditions for varying catalyst concentrations at molar ratio 4.5/1, 6/1 and 9/1 respectively. A significant increase in yield is noticed when the catalyst concentration is increased from 0.75% to 1% and the maximum yield is obtained at 1.5% catalyst for all molar ratios. An optimal yield of 96.1% is found to be obtained for the following reaction parameters: 9:1 molar ratio, 1.5% catalyst and 30 min reaction time. Figure 6.2 (a), (b) and (c) shows the variation of jatropha oil methyl ester yield as a function of time for ultrasonic irradiation at 10 bar pressure of reaction mixture for varying catalyst concentrations at molar ratio 4.5/1, 6/1 and 9/1 respectively. An optimum yield of 98.5% is obtained for the following reaction conditions: 6:1 molar ratio, 1% catalyst and 8 min reaction time. Figure 6.3 (a), (b) and (c) shows the variation of jatropha oil methyl ester yield as a function of time for ultrasonic irradiation at 15 bar pressure of reaction mixture for varying catalyst concentration at molar ratio 4.5/1, 6/1 and 9/1 respectively. An optimum yield of 99.2% is obtained for the following reaction conditions: 4.5:1 molar ratio, 0.75% catalyst and 3 min reaction time. Figure 6.4 (a), (b) and (c) shows the variation of jatropha oil methyl ester yield as a function of time for ultrasonic irradiation at 20 bar pressure of reaction mixture for varying catalyst concentrations at molar ratio 4.5/1, 6/1 and 9/1 respectively. An optimum yield of 99% is obtained for the following reaction conditions: 4.5:1 molar ratio, 0.5% catalyst and 2 min reaction time.

Table 6.1: Amount of oil, alcohol and catalyst used

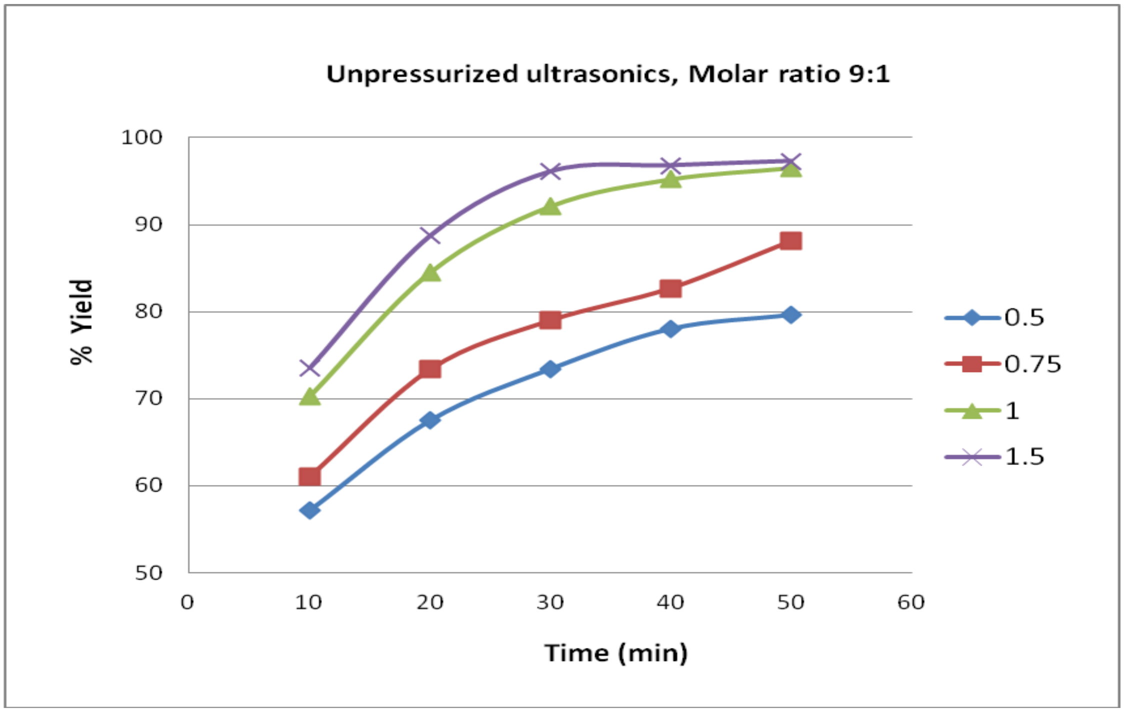
Molar Ratio	Catalyst (w/w oil)	Jatropha oil (kg)	Methanol (kg)	Catalyst (kg)
4.5:1	0.5	5	0.828	0.025
	1	5	0.828	0.05
	1.5	5	0.828	0.075
6:1	0.5	5	1.104	0.025
	1	5	1.104	0.05
	1.5	5	1.104	0.075
9:1	0.5	5	1.656	0.025
	1	5	1.656	0.05
	1.5	5	1.656	0.075



(a) Jatropha oil methyl ester yield for molar ratio 4.5:1

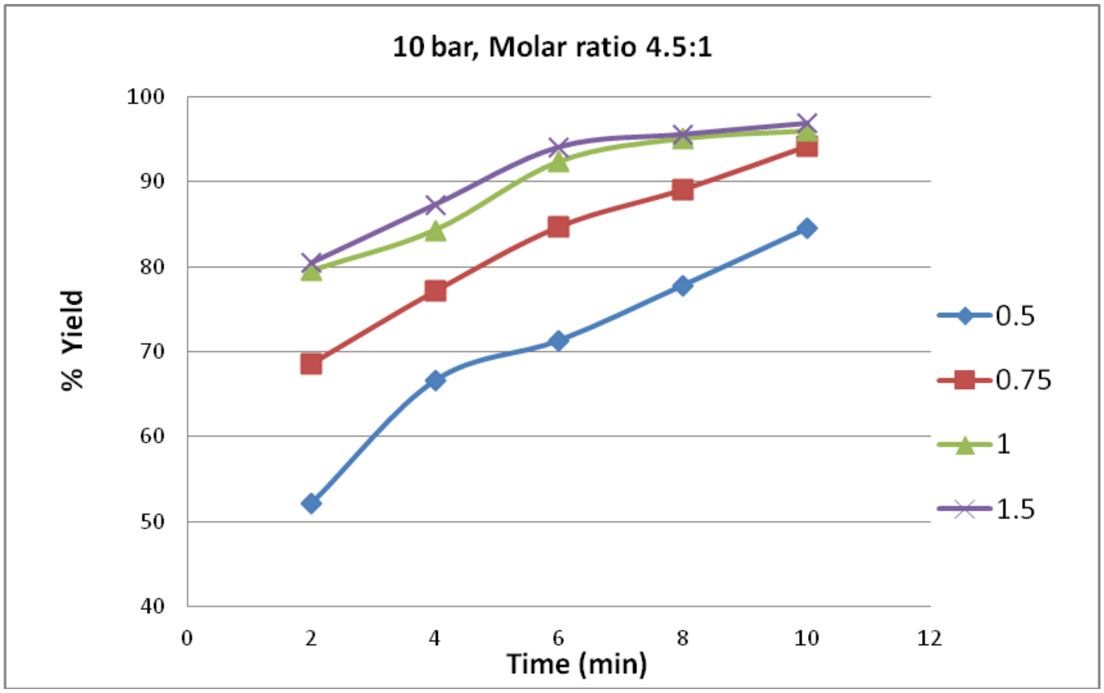


(b) Jatropha oil methyl ester yield for molar ratio 6:1

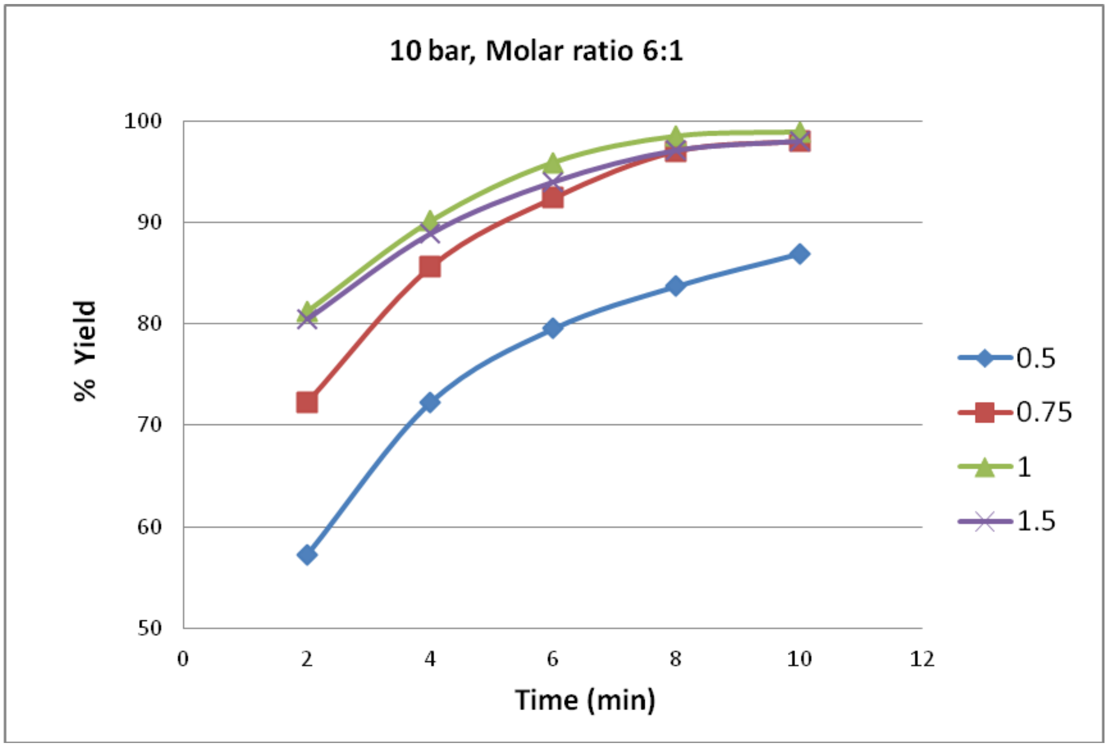


(c) Jatropha oil methyl ester yield for molar ratio 9:1

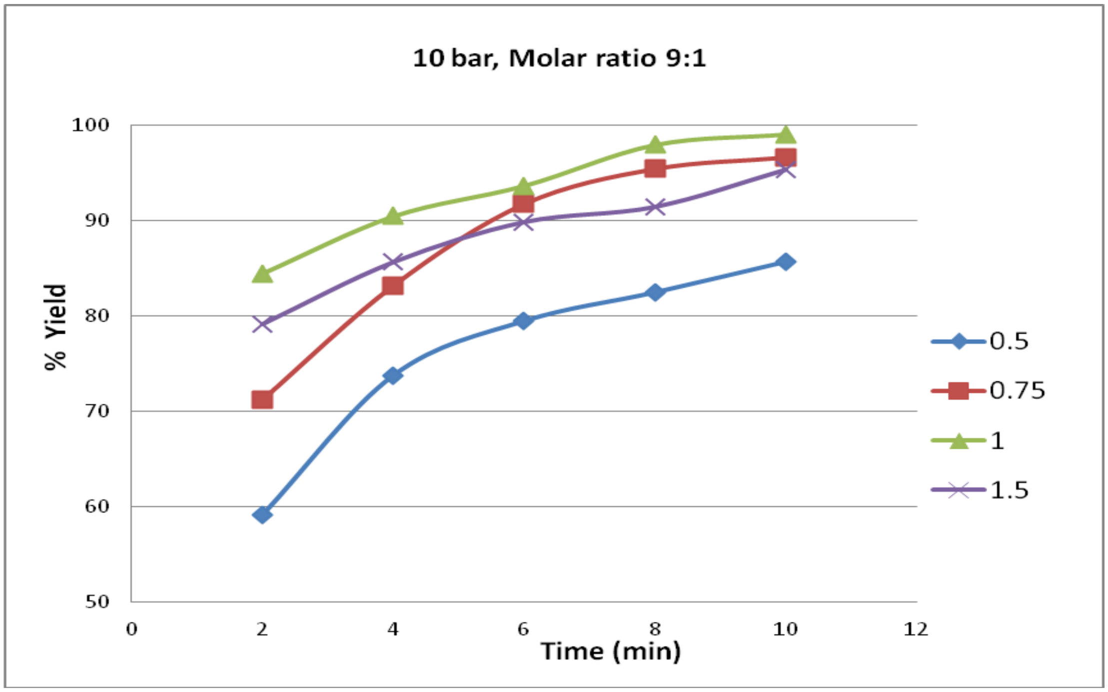
Fig. 6.1: Unpressurized ultrasonic cavitation



(a) Jatropha oil methyl ester yield for molar ratio 4.5:1

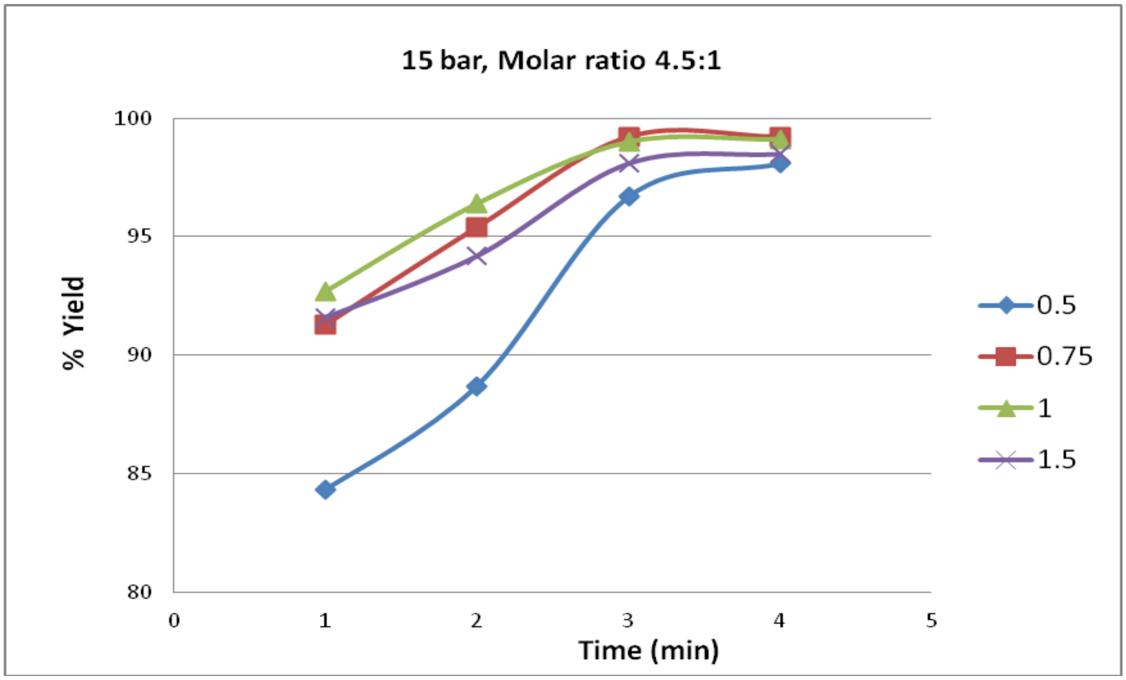


(b) Jatropha oil methyl ester yield for molar ratio 6:1

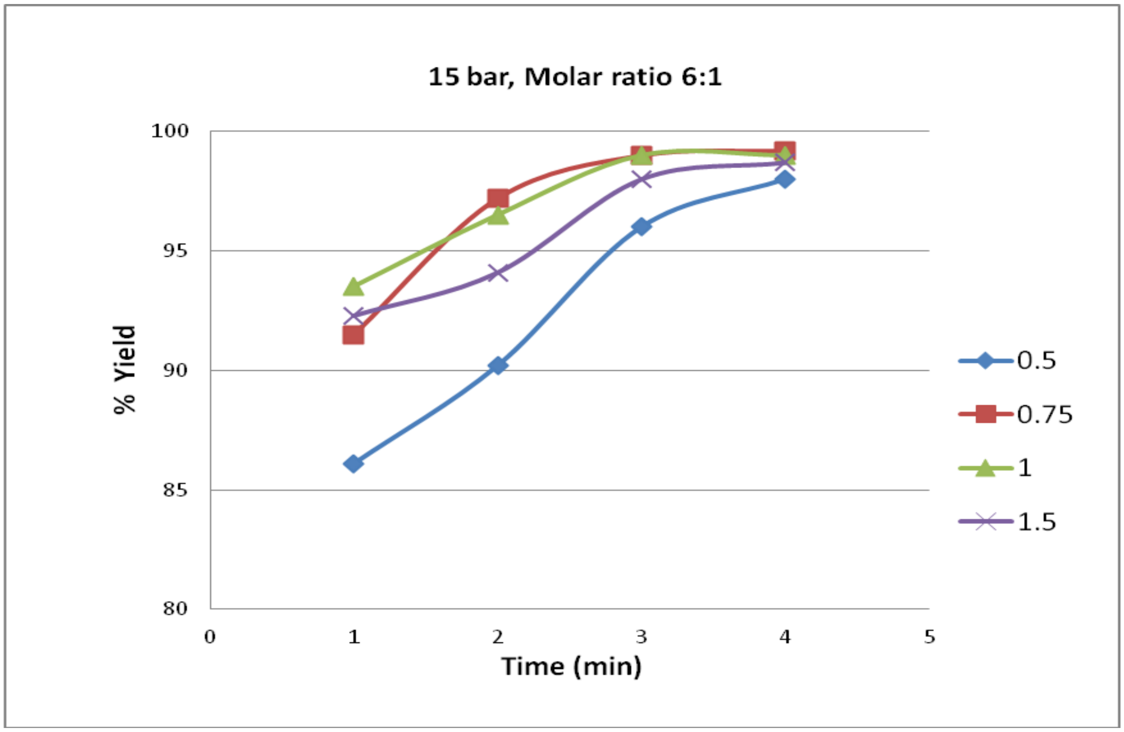


(c) Jatropha oil methyl ester yield for molar ratio 9:1

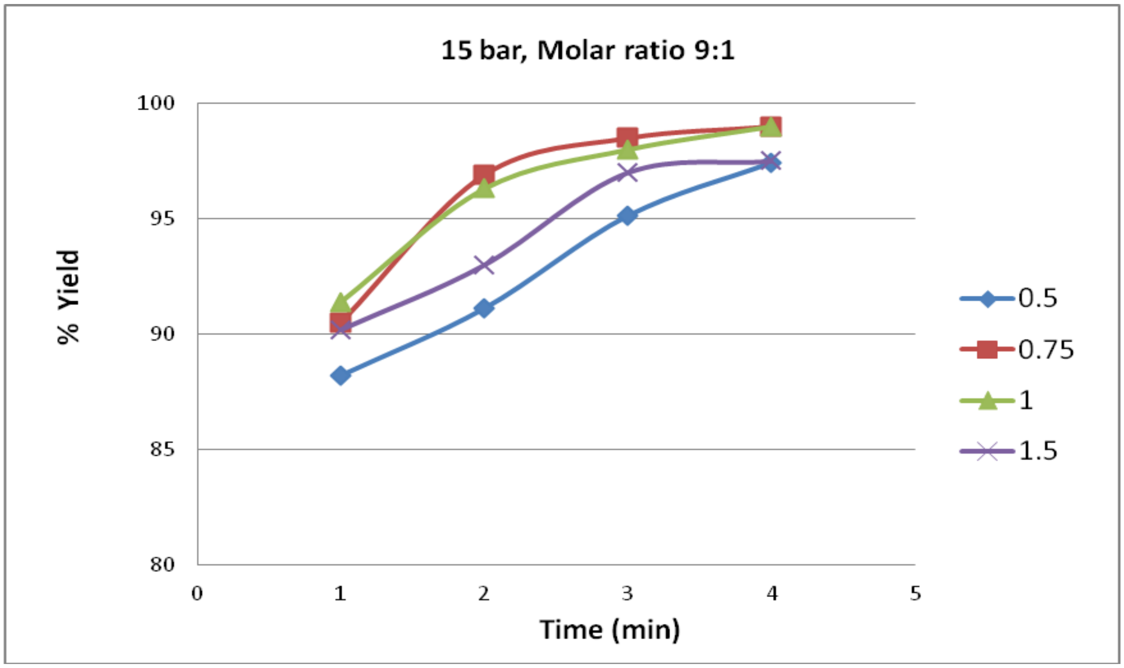
Fig. 6.2: Ultrasonic cavitation (10 bar)



(a) Jatropha oil methyl ester yield for molar ratio 4.5:1

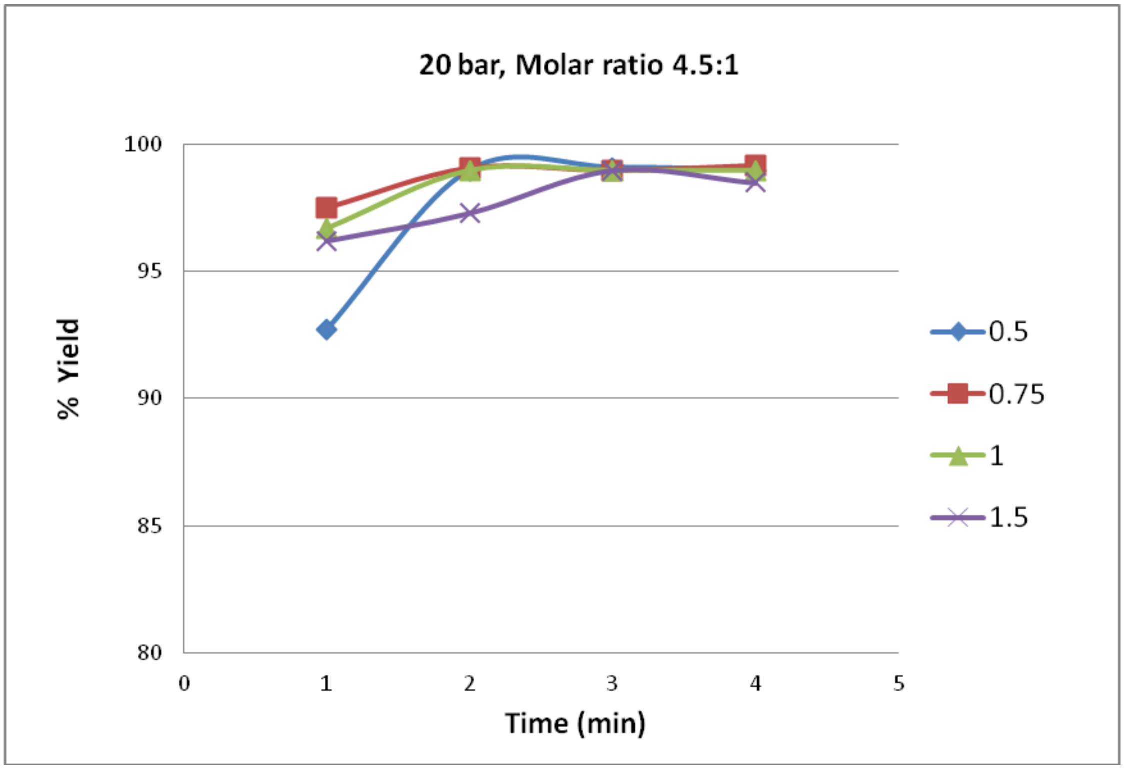


(b) Jatropha oil methyl ester yield for molar ratio 6:1

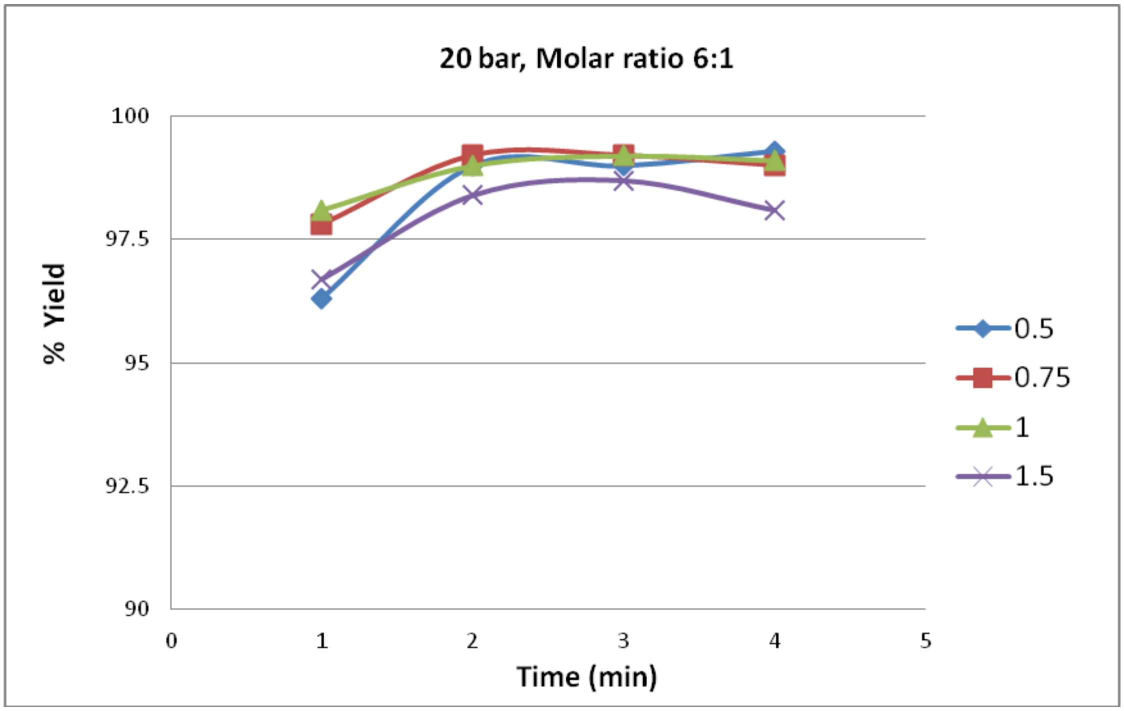


(c) Jatropha oil methyl ester yield for molar ratio 9:1

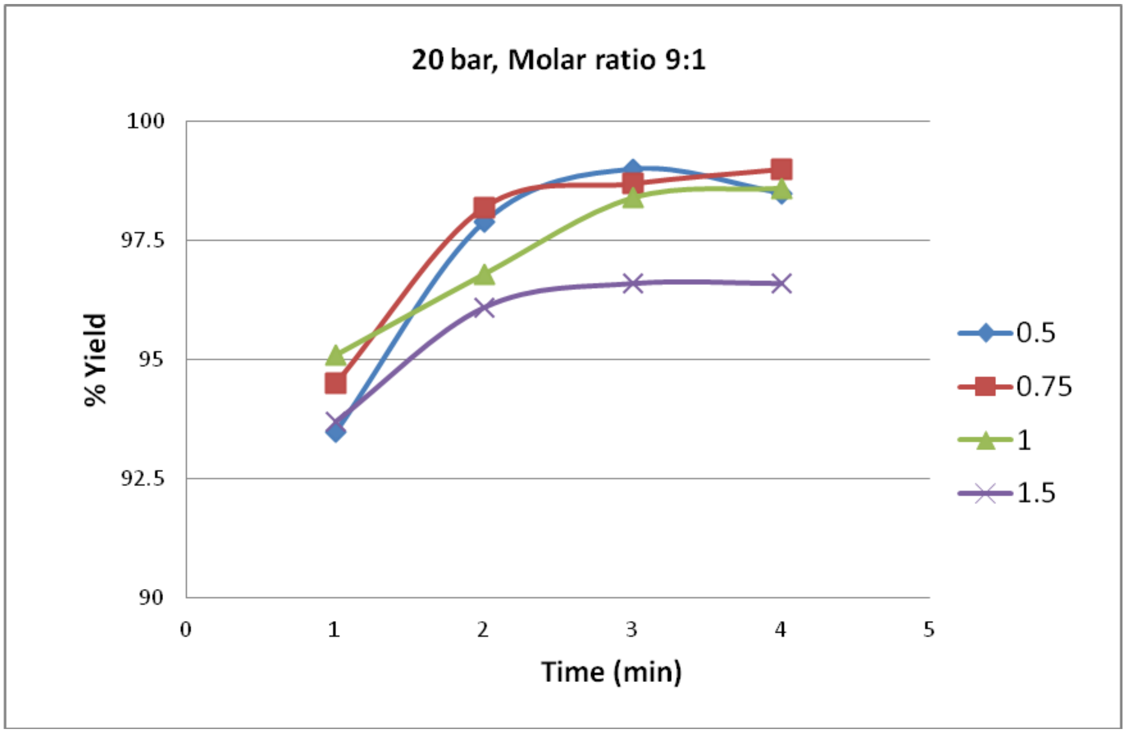
Fig. 6.3: Ultrasonic cavitation (15 bar)



(a) Jatropha oil methyl ester yield for molar ratio 4.5:1



(b) Jatropha oil methyl ester yield for molar ratio 6:1



(c) Jatropha oil methyl ester yield for molar ratio 9:1

Fig. 6.4: Ultrasonic cavitation (20 bar)

Comparing the reaction time for optimal yield, it can be noticed that reaction time for transesterification reduces considerably when ultrasonic irradiation takes place under pressurized conditions. Optimal reaction time at 10 bar pressure (8 min) is almost 27% of the optimal reaction time for unpressurized ultrasonic irradiation induced transesterification (30 min). Increasing the pressure of reaction mixture to 15 bar (3 min) reduces the optimal reaction time to almost 38% of the optimal reaction time when the reaction mixture is at 10 bar (8 min). Further increasing the pressure of reaction mixture does not have much impact on reaction time as shown from optimal reaction time of 3 min at 15 bar pressure as compared to 2 min at 20 bar pressure. In order to realize the effect of pressure in case of improved yield and reduced reaction time, a brief overview of ultrasound assisted reaction mechanism is presented here. Propagation of acoustic waves has both chemical and physical effect on the liquid-liquid heterogeneous reaction mixture. Chemical effect includes the generation of H^*, OH^* and HO^*_2 radicals during collapse of bubbles, which accelerates the chemical reaction in mixture (Hart et al., 1985; Hart et al., 1987). Physical effect includes the enhanced mass transfer and intimate mixing between the reactants associated with microturbulence due to radial motion of bubbles. Use of catalyst in sufficient quantity leads to generation of methoxide ions which is several times higher than ions generated by collapsing bubbles. Thus, we can interpret that the physical effect of ultrasonics (intensity of turbulence) is the deciding factor for the acceleration of reaction and the reaction yield. The intensity of turbulence generated by cavitating microscopic bubbles is a function of physical properties of the liquid medium such as density, viscosity, and surface tension. Moreover it also depends upon the amplitude of the acoustic wave and the pressure of mixture through which propagation of acoustic waves takes place (Kalva et al., 2009). The sharp decrease in reaction time is obtained due to increased intensity of energy release during collapse of bubbles and increased mass transfer due to enhanced micro-circulation when ultrasonic cavitation takes place in the reaction mixture at higher pressure. The enhanced intermixing of reaction mixture also leads to reduced requirement of catalyst and molar ratio for rapid transesterification.

6.4 Energy Analysis

Energy consumed in production of biodiesel in an ultrasonic reactor involves:

4. Energy required for heating the raw oil upto 110-120°C to remove the moisture content of oil.
5. Energy for maintaining the temperature of reaction mixture at 55-65°C.
6. Power provided to the ultrasonic transducers.
7. Power required by the pump to maintain the flow in closed loop circuit.

The energy required to remove the moisture content of raw oil and to maintain the reaction mixture at 55-65°C is insignificantly small in comparison to the overall energy consumption of the biodiesel production process. Hence, these energies are neglected while calculating SEC and EUI of biodiesel produced. Table 6.2 shows the analysis and comparison of energy consumption under unpressurized and pressurized ultrasonic irradiation conditions. Biodiesel synthesis under pressurized ultrasonic irradiation condition showed significantly higher energy efficiency in comparison to biodiesel synthesis under unpressurized ultrasonic irradiation condition. SEC and EUI showed favorable trends with increasing power of the reaction mixture. However the decrease in SEC and increase in EUI are significant when the pressure is increased upto 15 bar (SEC 0.018 and EUI 589.83) and thereafter the gain in economic feasibility is nominal with increasing pressure (SEC 0.015 and EUI 681.37 at 20 bar). Ultrasonic irradiation under pressurized condition with pressure ranging from 15-20 bars has an additional advantage of rapid reaction rate that makes it most suitable method of biodiesel synthesis.

6.5 Property Testing

Property testing and characterization of biodiesel produced closed loop ultrasonic reactor operating at 20 bar was done and various physio chemical properties of Jatropha oil methyl esters were found to lie within acceptable limits (except oxidative stability) as shown in Table 6.3. Oxidative stability can be improved by adding suitable antioxidants.

Table 6.2: Analysis of Specific Energy Consumption and Energy Unit Index

Pressure conditions	Mass of Biodiesel (kg)	Transducer Power (W)	Pump Power (W)	Time (min)	Energy Consumed (kWh)	SEC (kWh/kg)	LCV (J/g)	EUI
Non-pressurized	$5\times\frac{96.1}{100}=4.805$	$2(0.7\times400)=560$	465	30	0.510	0.102	37,042	96.94
10 bar	$5\times\frac{98.5}{100}=4.925$	$2(0.7\times400)=560$	985	8	0.206	0.042	37, 251	247.38
15 bar	$5\times\frac{99.2}{100}=4.96$	$2(0.7\times400)=560$	1205	3	0.088	0.018	37,673	589.83
20 bar	$5\times\frac{99}{100}=4.95$	$2(0.7\times400)=560$	1720	2	0.076	0.015	37,661	681.37

Table 6.3: Properties of biodiesel

Property	**Acceptable limits**	**Biodiesel (20 bar)**
Cetane Number	Min: 51	64.3
Density at 15°C (kg/m^3)	860-900	887
Viscosity at 40°C (mm^2/s)	3.5-5	4.35
Higher Calorific Value (J/g)		38,990
Flash Point (°C)	Min. 120	166
Cold Filter Plugging Point, CFPP (^{0}C)		6
Oxidative Stability	Min 6	3.23

6.6 Conclusions

Optimization and energy analysis of biodiesel production from jatropha oil under unpressurized and pressurized ultrasonic irradiation condition is carried out successfully and the following conclusions are drawn from the experimental investigations. The optimal reaction conditions obtained for transesterification through unpressurized ultrasonic irradiation are: 9:1 molar ratio, 1.5% catalyst and 30 min reaction time with maximum yield of 96.1%. The optimal reaction conditions obtained for reaction mixture at 10 bar pressure are: 6:1 molar ratio, 1% catalyst and 8 min reaction time with maximum yield of 98.5%. The optimal reaction conditions obtained for reaction mixture at 15 bar pressure are: 4.5:1 molar ratio, 0.75% catalyst and 3 min reaction time with maximum yield of 99.2%. The optimal reaction conditions obtained for reaction mixture at 20 bar pressure are: 4.5 molar ratio, 0.5% catalyst and 2 min reaction time with maximum yield of 99%. SEC for unpressurized ultrasonic cavitation, ultrasonic irradiation at 10 bar, 15 bar and 20 bar pressure are 0.102, 0.042, 0.018 and 0.015 respectively. EUI for unpressurized ultrasonic cavitation, ultrasonic irradiation at 10 bar, 15 bar and 20 bar pressure are 96.94, 247.38, 589.83 and 681.37 respectively. Lower requirement of catalyst and alcohol to oil molar ratio, lower energy consumption, higher value of EUI, simpler purification of products and rapid reaction rate at 15-20 bar pressure of reaction mixture makes it the most economically viable condition for biodiesel production.

CHAPTER 7

ECONOMIC ANALYSIS OF BIODIESEL PRODUCTION

7.1 Introduction

In the present work, cost of biodiesel production from Jatropha oil in a closed loop pressurized ultrasonic reactor under optimal conditions was calculated to analyze economic feasibility of biodiesel production. From the experimental investigations and energy analysis of biodiesel production, it was found that the minimum specific energy consumption (0.015) was obtained at 20 bar pressure as shown in Table 6.2. 99% biodiesel yield was obtained in 2 mins reaction time for a 5kg sample of Jatropha oil. However the tank capacity is 5-50 kg and economic analysis was carried out for a batch size of 40 kg oil, considering processing of 40 batches per day. Optimal yield of 99% was obtained in 4.5 mins reaction time for 40 kg batch size with SEC of 0.038 (Transducers operating at 70% of rated power) as shown in Table 7.1.

Table 7.1: SEC for 40 kg Sample

Pressure conditions	Mass of Biodiesel (kg)	Transducer Power (W)	Pump Power (W)	Time (min)	Energy Consumed (kWh)	SEC (kWh /kg)
20 bar	$5\times\frac{99}{100}=4.95$	$2\left(0.7\times400\right)=560$	1720	4.5	0.171	0.038

7.2 Specifications

Motor Power for stirring alcohol and catalyst = 0.18 kW

Heater (from removing moisture from raw oil) Power = 1 kW

Heater (used for heating water in water washing step) Power = 1 kW

Heater (used for drying the biodiesel produced) Power = 1 kW

Motor Power for stirring hot water and biodiesel for water washing step = 0.18 kW

Rated Power of Transducers = 0.4 kW

Rated power of reciprocating pump for establishing flow in closed loop reactor = 3 hp

Heating efficiency (due to heat losses) assumed = 90%

1KWh of electricity = Rs. 8/- (for industrial use)

Specific heat of Jatropha oil and its methyl esters = 2 kJ/kg K (assumed)

Specific heat of water = 4.2 kJ/kg K

Total working days per month = 25

7.3 Electricity Cost

- Heating raw oil from 20^{o}C to about 120^{o}C per batch.

$$Q = \frac{m \times c \times \Delta T}{\eta_{\text{heating}}}$$

$$= \frac{40 \times 2 \times 100}{0.9}$$

$$= 8888.89 \text{ kJ}$$

$$\text{Heating duration} = \frac{8888.89 \text{ kJ}}{1 \text{ kW}} = 8888.89 \text{ sec} = 148.15 \text{ mins (approx.)}$$

$$\text{Electricity cost / batch} = \frac{148.15}{60} \times 1 \times 8 = 19.75 \text{ Rs}$$

$$\text{Electricity cost / month} = 19.73 \times 40 \times 25 = 19734 \text{ Rs}$$

- Stirring alcohol and catalyst

Stirring duration = 10 mins

Electricity cost / batch $= \frac{10}{60} \times 0.18 \times 8 = 0.24$ Rs

Electricity cost / month $= 0.24 \times 40 \times 25 = 240$ Rs

- Ultrasonic irradiation

Electricity cost / batch = Time × Transducer Power × Cost/kWhr

$$= \frac{4.5}{60} \times \left(2 \times \left(0.7 \times \frac{400}{1000}\right)\right) \times 8$$

$= 0.336$ Rs

(Two transducers operating at 70% of the rated power)

Electricity cost / month $= 0.336 \times 40 \times 25 = 336$ Rs

- Maintaining flow in a closed loop reactor with the help of reciprocating pump at 20 bar pressure

Electricity cost / batch = Time × Power utilized in reciprocating pump × Cost/kWhr

$$= \frac{4.5}{60} \times \left(\frac{1720}{1000}\right) \times 8$$

$= 1.032$ Rs

Electricity cost / month $= 1.032 \times 40 \times 25 = 1032$ Rs

- Heating water from 20^{o}C to about 60^{o}C for water washing

$$\text{Q (12 kg Batch)} = \frac{m \times c \times \Delta T}{\eta_{heating}}$$

$$= \frac{12 \times 4.2 \times 40}{0.9}$$

$= 2240$ kJ

Heating duration $= \frac{2240 \text{ kJ}}{1 \text{ kW}} = 2240$ sec = 37.33 mins

Electricity cost / batch $= \frac{37.33}{60} \times 1 \times 8 = 5$ Rs (approx)

Electricity cost / month $= 5 \times 40 \times 25 = 5000$ Rs

- Stirring biodiesel with hot water for water washing step

Electricity cost / batch = Time (hrs) × Motor power for stirring (kW) × Cost/kWhr

$$= \frac{3}{60} \times 0.18 \times 8$$

$$= 0.072 \text{ Rs}$$

Electricity cost / month $= 0.072 \times 40 \times 25$ = 72 Rs

- Heating biodiesel from 20 °C to about 120°C for removing water if present

$$Q = \frac{m \times c \times \Delta T}{\eta_{heating}}$$

$$= \frac{(0.99 \times 40) \times 2 \times 100}{0.9}$$

$$= 8800 \text{ kJ}$$

Heating duration $= \frac{8800 \text{ kJ}}{1 \text{ kW}} = 8800$ sec = 148 mins (approx.)

Electricity cost / batch $= \frac{1448}{60} \times 1 \times 8 = 19.73$ Rs

Electricity cost / month $= 19.73 \times 40 \times 25$ = 19740 Rs

Total electricity cost involved per month = (19,734 + 240 + 336 + 1,032 + 5000+ 72 + 19,740) Rs = 46154 Rs

7.4 Apparatus cost

Total cost of apparatus and equipments is about 285,000 Rs

Assuming these equipments works for 10 yrs and taking 8% interest rate

Equipment cost for a month = 4275 Rs

7.5 Miscellaneous cost

Miscellaneous cost is as shown in Table 7.2.

Table 7.2: Miscellaneous Cost

Purpose	Cost per month (Rs)
Transportation Cost	15,000
Labour Cost	1 Semi skilled (15,000) 1 Skilled (20,000) 1 Supervisor (20,000)
Rent Cost	10,000
Maintenance Cost	5,000

Total Miscellaneous Cost = 85,000 Rs / month

7.6 Biodiesel Production Cost Per kg

Total biodiesel produced / month = $0.99\left(40 \times 40 \times 25\right)$ = 39,600 Rs

Total processing cost / month = 46,154 + 4,275 + 85,000 = 135,429 Rs

Processing cost / kg = $\frac{135{,}429}{39{,}600}$ = 3.42 Rs

CHAPTER 8

CONCLUSIONS AND SCOPE OF FUTURE WORK

8.1 Major Findings

The following major findings have been drawn from the present study on the basis of experimental investigation.

1. Jatropha oil methyl esters were stable at atmospheric conditions and various physio-chemical properties were found to lie within acceptable limits, except for oxidative stability. Oxidative stability can be easily improved by use of suitable antioxidants.
2. Triple frequency flow cell ultrasonic reactor is investigated to be the best reactor (for laboratory size small scale production) for energy consumption and economic worth for biodiesel synthesis due to its minimum SEC (0.043 kWh/kg) and maximum EUI (243.54) respectively. Triple frequency flow cell ultrasonic reactors have additional advantage of rapid reaction rate which makes it most suitable ultrasonic reactor for biodiesel synthesis. Double frequency flow cell can also be considered as a highly energy efficient reactor for biodiesel synthesis because of its low SEC of 0.065 kWh/kg and high EUI of 162.1.
3. Closed loop combined process reactor is more economical, reliable and energy efficient as compared to closed loop ultrasonic reactor and closed loop mechanical stirrer. Combined process reactor has additional advantages of lower reaction time, lower requirement of catalyst and lower requirement of alcohol to oil molar ratio.

4. Biodiesel yield is a strong function of transducer power. Reaction rate increases with increase in power of ultrasonic irradiation, achieves a maximum value and thereafter shown a slight decline in reaction rate and biodiesel yield.
5. Ultrasonic cavitation in the reaction mixture at pressures above atmospheric pressure shows significant improvement in rate of transesterification. Lower requirement of catalyst and alcohol to oil molar ratio, lower energy consumption, higher value of EUI, simpler purification of products and rapid reaction rate at 15-20 bar pressure of reaction mixture makes it the most economically viable condition for biodiesel production.
6. Biodiesel production is economically viable. Cost of biodiesel production from jatropha oil in pressurized ultrasonic reactor under optimal conditions is approximately 3.5 Rs per kg

8.2 Scope of Future Work

The following points are recommended for future work, for biodiesel production.

1. Various High FFA non edible oils can be explored for biodiesel production in closed loop ultrasonic and combined process reactor.
2. Use of Hydrodynamic cavitation along with ultrasonic irradiation in closed loop reactor can be studied for biodiesel production.
3. Use of multiple transducers with different frequencies can be analyzed in pressurised ultrasonic production of biodiesel in a closed loop reactor.
4. Experimental results can be compared with the results obtained from optimization techniques such as Taguchi method and Response Surface Methodology.

5. Closed loop reactors can be tested for larger sample sizes, suitable for large scale industrial production.

REFERENCES

Abbaszaadeh A, Ghobadin B, Omidkhah M R and Najafi G (2012) Current biodiesel production technologies: a comparitive review. Energy Conservation and Management. 63:138-148.

Abbaszaadeh A, Masjuki H, Mahila T, Ong H, Chong W and Boosroh M (2013) Experimental study on performance and exhaust emissions of a diesel engine fuelled with Ceiba pentandra biodiesel blends. Energy Conversation and Management. 76: 828-836.

Agarwal A K (1998) Vegetable oil versus diesel fuel: development and use of biodiesel in a compression ignition engine. Teri Information Digest on Energy and Enviourment. 8(3): 191–204.

Agarwal A K and Das L M (2001) Biodiesel development and characterization for use as a fuel in compression ignition engine. Journal of Engineering Gas Turbines and Power. 123: 440–7.

Agarwal A K (2007) Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Progress in Energy and Combustion Science. 33:233–271.

Agarwal A K, Rajamanoharan K (2009) Experimental investigations of performance and emissions of Karanja oil and its blends in a single cylinder agricultural diesel engine. Applied Energy. 86: 106–112.

Aggarwal M, Singh K, Upadhyaya S and Chaurasia S P (2012) Potential vegetable oils of Indian Origin as biodiesel feedstock – An experimental study. Journal of Scientific and Industrial Research. 12: 285-289.

Akintayo E T (2004) Characterstics and composition of Parkia biglobbossa and jatropha curcas oils and cakes, Bioresource Technology, 92: 307-310.

Alhassan Y, Kumar N, Bugaje I M, Pali H S and Kathkar P (2014) Co-solvents transesterification of cotton seed oil into biodiesel: Effects of reaction conditions on quality of fatty acids methyl esters. Energy Conversion and Management. 84:640-648.

Amoroso A, Beine H J, Sparapani R, Nardino M and Allegrini (2006) Observation of coinciding arctic boundary layer ozone depletion and snow surface emissions of nitrous acid. Atmospheric Environment. 40: 1949–56.

Antolın G, Tinaut F V, Briceno Y, Castano V, Perez C and Ramırez A I (2002) Optimisation of biodiesel production by sunflower oil transesterification. Bioresource Technology. 83: 111-114.

Atadashi I M, Aroua M K and Abdul A A (2010) High quality biodiesel and its diesel engine application: A review. Renewable and Sustainable Energy Reviews. 14: 1999-2008.

Baddy A S, Abdullah A Z and Lee K T (2013) Optimization of biodiesel production from Jatropha oil using supported hetropolyacid catalyst and assisted by ultrasonic energy. Renewable Energy. 50: 427-432.

Balat M and Balat H (2008) Progress in biodiesel processing. Applied Energy. 49: 2727-2741.

Balat M and Balat H (2008) A critical review of bio-diesel as a vehicular fuel. Energy Conversion and Management. 49: 2727-2741.

Balat M (2011) Potential alternatives to edible oils for biodiesel production - A review of current work. Energy Conversion and Management. 52: 1479-1492.

Barbosa S L, Dabdoub M J, Hurtado G R, Klein S I, Baroni A C M and Cunha C (2006) Solvent free esterification using Lewis acids in solid phase catalysis. Applied Catalysis A: General. 313(2): 146-150.

Barnwal B K and Sharma M P (2005) Prospects of biodiesel production from vegetable oils in India. Renewable and Sustainable Energy Reviews. 9: 363–378.

Bastante J S, Pinzi S, Romero F J J, Castro M D L D, Capote F P and Dorado M P (2015) Synthesis of biodiesel from castor oil: Silent versus sonicated methylation and energy studies. Energy Conservation and Management. 96: 561-567.

Betiku E and Ajala S O (2014) Modeling and optimization of Thevetia peruviana (yellow oleander) oil biodiesel synthesis via Musa paradisiacal (plantain) peels as heterogeneous base catalyst: A case of artificial neural network vs. response surface methodology. Industrial Crops and Products. 53: 314-322.

Bojan S G, Chelladurai S and Durairaj S K (2011) Response Surface Methodology for optimization of biodiesel production from high FFA Jatropha Curcas Oil. International Journal of Green Energy. 8: 607-617.

Bokhari A, Chuah L F, Yusup S, Klemeš J J, Akbar M M and Kamil R N M (2016) Cleaner Production of Rubber Seed Oil Methyl Ester using a Hydrodynamic Cavitation: Optimisation and Parametric Study. Journal of Cleaner Production. 136: 31-41.

Boulifi N E, Bouaid A, Martinez M and Aracil J (2013) Optimization and oxidative stability of biodiesel production from rice bran oil. Renewable Energy. 53: 141-147.

BP Energy Outlook (2017) "https://www.bp.com/content/dam/bp/pdf/energy-economics/energy-outlook-2017/bp-energy-outlook-2017.pdf" accessed on 20 Nov 2017.

BP Statistical Review of World Energy (2016) "http://www.bp.com/content/dam/bp/pdf/energyeconomics/statistical-review-2016/bp-statistical-review-of-world-energy-2016-full report.pdf" accessed on 10 August 2017.

Chadda P, Arora A K, Prakash S, Jha M K, Puri S K, Tuli D K and Malhotra R K (2012) Ultrasonic assisted in situ transesterification of Jatropha seed to biodiesel. Journal of Scientific and Industrial Research. 71: 290-294.

Choudhury H A, Goswami P P, Malani R S and Moholkar V S (2014) Ultrasonic biodiesel synthesis from crude Jatropha curcas oil with hetrogeneous base catalyst: Mechanist insight and statistical optimization. Ultrasonic Sonochemistry. 21: 1050-1064.

Colucci J, Borrero E and Alape F (2005) Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing. Journal of the American Oil Chemist's Society. 82: 525-30.

Deka D C and Basumatary S (2011) High quality biodiesel from yellow oleander (Thevetia peruviana) seed oil. Biomass and Bioenergy. 35: 1797-1803.

Demirbas A (2002) Biodiesel from vegetable oils via transesterification in supercritical methanol. Energy Conversation and Management. 43:2348-56.

Demirbas A (2003) Biodiesel fuels from vegetable oils via catalytic and non catalytic supercritical alcohol transesterification and other methods: a survey. Energy Conversation and Management. 44: 2093-109.

Demirbas A (2005) Biodiesel production from vegetable oils by supercritical methanol. Journal of Scientific & Industrial Research. 64: 858-865.

Demirbas A (2006) Biodiesel production via non- catalytic SCF method and biodiesel fuel characterstics. Energy Conversation and Management. 47: 2271-2282.

Demirbas A (2008) Progress and recent trends in biodiesel fuel. Energy Conversion and Management. 16: 14–34.

Demirbas A (2009) Progress and recent trends in biodiesel fuels. Energy Conversion and Management. 50:14–34.

Devanesan M G, Viruthagiri T and Sugumar N (2007) Transesterification of Jatropha oil using immobilized Pseudomonas fluorescens. African Journal of Biotechnology. 6(21): 2497-2501.

Dos Santos V M L, Da Silva J A B, Stragevitch L and Longo R L (2011) Thermochemistry of biodiesel oxidation reactions: a DFT study. Fuels. 90: 811-817.

Endalew A K, Kiros Y and Zanzi R. 2011. Heterogeneous catalysis for biodiesel production from Jatropha curcas oil (JCO). Energy. 1-8.

Energy Information Administration, International Energy Outlook (2016) "https://www.eia.gov/outlooks/ieo/pdf/transportation.pdf" accessed on 17 August, 2017.

Eneegy Statics, Ministry of statistics and programme implementation (2017) "http://www.mospi.nic.in/sites/default/files/publication_reports/EnergyStatistics_2017r.pdf.pdf" accessed on 28 August, 2017

Foidl N, Foidl G, Sanchez M, Mittelbach M and Hackel S (1996) Jatropha curcas L. as a source for the production of biofuels in Nicaragua. Bioresource Technology. 58: 72-82.

Freedman B, Pryde E H and Mounts T L (1984) Variables affecting the yields of fatty esters from transesterified vegetable oils. Journal of the American oil Chemist's Society. 61: 1638–43.

Gendy N S E, Deriase S F and Hamdy A (2014) The optimization of Biodiesel production from Waste Frying Corn oil using Snails as a Catalyst. Energy Sources, Part A. 36: 623-637.

Ghazali W, Nor M W, Mamat R , Masjuki H H, Najaf G (2015) Effects of biodiesel from different feed stocks on engine performance and emissions: A review. Renewable and Sustainable Energy Reviews. 51:585–602.

Gogate P R and Pandit A B (2005) A review and assessment of hydrodynamic cavitation as a technology for the future. Ultrasonics Sonochemistry. 12(1): 21–27.

Gogate P R, Tayal R K and Pandit A B (2006) Cavitation: A technology on horizon. Current Science. 91: 35-46.

Gude V G and Grant G E (2013) Biodiesel from waste cooking oil via direct sonification. Applied Energy. 109: 135-144.

Guerra E M and Gude V G (2015) Continuous and pulse sonication effects on transesterification of used vegetable oils. Energy Conservation and Management. 96: 268-76.

Gui M M, Lee K T and Bhatia S (2008) Feasibility of edible oil vs non-edible oil vs waste edible oil as biodiesel feedstock. Energy. 33: 1646–53.

Hanh H D, Dong N T, Starvarache C, Okitsu K, Maeda Y and Nishimura R (2008) Methanolysis of Triolein by low frequency ultrasonic irradiation. Energy Conservation and Management. 49: 276-280

Hanh H D, Dong N T, Starvarache C, Okitsu K, Maeda Y and Nishimura R (2009) Biodiesel production through transesterification of triolein with various alcohols in an ultrasonic field. Renewable Energy. 34: 766-768.

Han H D, Nguyen T D, Okistu K, Nishimura R and Maeda Y (2009) Biodiesel production by esterification of oleic acid with short-chain alcohols under ultrasonic irradiation condition. Renewable Energy. 34: 780-783.

Han H, Cao W and Zhang J (2005) Preparation of biodiesel from soybean oil using supercritical methanol and CO_2 as co-solvent. Process Biochemistry. 40: 3148-51.

Hart E J and Henglein A (1985) Free Radical and Free Atom Reactions in the Sonolysis of Aqueous Iodide and Formate Solutions. The Journal of Physical Chemistry. 89: 4342.

Hart E J and Henglein A (1987) Sonochemistry of Aqueous Solutions: Hydrogen- Oxygen Combustion in Cavitation Bubbles. The Journal of Physical Chemistry. 91: 3654.

Harwood H J (1984) Oleochemicals as a fuel: Mechanical and economic feasibility. Journal of the American oil Chemist's Society. 61: 315–24.

Hoda N (2010) Optimization of Biodiesel production from Cottonsed oil by transesterification using NaOH and Methanol. Energy Sources, Part A. 32: 434-441.

Ji J, Wang J, Yongchao L, Yunliang Y and Zhichao X (2006) Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. Ultrasonics. 44: 411-

414.

Joshi G , Rawat D S, Lamba B Y, Bisht K K, Kumar P, Kumar N and Kumar S (2015) Transesterification of Jatropha and Karanja oils by using waste egg shell derived calcium based mixed metal oxides. Energy Conservation and Managment. 96: 258-267.

Kalva A, Sivasankar T and Moholkar V S (2009) Mechanism of Ultrasound-Assisted Synthesis of Biodiesel. Industrial and Engineering Chemistry Research. 48: 534–544.

Kandpal J B and Madan M (1995) Jatropha curcus: a renewable source of energy for meeting future energy needs. Renewable Energy. 6: 159-160.

Kaur M and Ali A (2011) Lithium ion impregnated calcium oxide as nano catalyst for the production from karanja and jatropha oils. Renewable Energy. 36: 2866-2871.

Kawashima A. Matsubara K and Honda K (2009) Acceleration of catalytic activity of calcium oxide for biodiesel production. Bioresource Technology. 100: 696-700.

Kiakalaieh A T, Amin N A S, Zarei A and Jaliliannosrati H (2013) Biodiesel production from High Free Fatty acid Waste Cooking Oil by Solid Acid Catayst. International Conference on Process System Engineering. 6: 25-27.

Kumar D, Kumar G, Poonam C and Singh C P (2010) Ultrasonic assisted transesterification of Jatropha curcus oil using solid catalyst, Na/SiO. Ultrasonic Sonochemistry. 17: 839-44.

Kusdiana D and Saka S (2001) Kinetics of transesterification in rapeseed oil to biodiesel fuels as treated in supercritical methanol. Fuels. 80:693-698.

Lapuerta M, Armas O, Fernandez J R (2008) Effect of biodiesel fuels on diesel engine emissions. Progress in Energy and Combustion Science. 34:198–223.

Lapuerta M, Herrero J M, Lyons L L, Contreras R G, Briceño Y (2008) Effect of the alcohol type used in the production of waste cooking oil biodiesel on diesel performance and emissions. Fuels. 87: 3161–3169.

Leduc S, Natarajan K, Dotzauer E, McCallum I and Obersteiner M (2009) Optimizing Biodiesel production in India. Applied Energy. 86: S125-S131.

Lee S B, Lee J D and Hong I K (2011) Ultrasonic energy effect on vegetable oil based biodiesel synthetic process. Journal of Industrial Engineering and Chemistry. 17: 138-143.

Leung D Y C, Wu X and Leung M K H (2010) A review on biodiesel production using catalyzed transesterification. Applied Energy. 87: 1083-1095

Levander T (1990) The relative contributions to the greenhouse effect from the use of different fuels. Atmospheric Environment. 24: 2707–14.

Lin B F, Huang J H and Huang DY (2009) Experimental study of the effects of vegetable oil methyl ester on DI diesel engine performance characteristics and pollutant emissions. Fuels. 88: 1779–85.

Li S, Wang Y, Dong S, ChenY, Cao F , Chai F and Wang X. 2009. Biodiesel production from Eruca Sativa Gars vegetable oil and motor, emissions properties. Renewable Energy. 34: 1871–1876.

Ma F and Hanna M A (1999) Biodiesel production: a review. Bioresource Technology. 70:1–15.

Ministry of Petroleum and Natural Gas, Govt. of India (2009) "www.petroleum.nic.in./petstat.pdf" Accessed on 30 November, 2017.

Moholkar V S, Rekveld S and Warmoeskerken M M C G (2000) Modeling of the acoustic pressure fields and the distribution of the cavitation phenomena in a dual frequency sonic processor. Ultrasonics. 38: 666-670.

Mosarof M H, Kalam M A, Masjuki H H, Ashraful A M, Rashed M M, Imdadul H K and Monirul I M (2015) Implementation of palm biodiesel based on economic aspects, performance, emission, and wear characteristics. Energy Conservation and Management. 105: 617-629.

Moser B R(2009) Biodiesel production, properties and feedstocks. Biofuels. 45: 229-266.

Murugesan A, Umarani C, Chinnusamy T R, Krishnan M, Subramanian R and Neduzchezhain N. 2009. Production and analysis of bio-diesel from non-edible oils - A review. Renewable and Sustainable Energy Reviews. 13: 825-834.

Nishimura C S M V and Maeda Y R (2003) Conversion of vegetable oil to biodiesel using ultrasonic irradiation. Chemistry Letters. 32: 716-717.

Noiroj K, Intarapong P, Luengnaruemitchai A and Jai-In S (2009) A comparative study of KOH/Al_2O_3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. Renewable Energy. 34:1145–1150.

Pal A, Kachhwaha S S, Maji S and Babu M K G (2010) Thumba seed oil: A sustainable source of renewable energy for biodiesel production. Journal of Scientific and Industrial Research. 69:384-389.

Pal A, Verma A, Kachhwaha S S and Maji S (2010) Biodiesel production through hydrodynamic cavitation and performance testing. Renewable Energy. 35: 619–624.

Patle D S, Sharma S, Ahmad Z and Rangaiah G P (2014) Multi-objective optimization of two alkali catalyzed processes for biodiesel from waste cooking oil. Energy Consevation and Managment. 85: 361-372.

Pereira J P, Nakatani J, Kurisu K and Hanaki K (2016) Life cycle assessment of conventional and optimised Jatropha biodiesel Fuels. Renewable Energy. 86:585-593.

Planning Commission Report, India (2003)

Pramanik K (2003) Properties and use of Jatropha curcas oil and diesel fuel blends in compression ignition engine. Renewable Energy. 28: 239–48.

Rahimi M, Aghel B, Alitabar M, Sepahvand A and Ghasempour H R (2014) Optimization of biodiesel production from soybean oil in a microreactor. 79: 599-605.

Rabua R A, Janajreha I and Honnery D (2013) Transesterification of waste cooking oil: Process optimization and conversion rate evaluation. Energy Consrvation and Managmaent. 66: 764-769.

Sajid Z, Khan F and Zhang Y (2016) Process simulation and life cycle analysis of biodiesel production. Renewable Energy. 85:945-952.

Saka S and Kusiana D (2001) Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. Fuels. 80: 225-31.

Sarin R, Sharma M, Sinharay S and Malhotra R K (2007) Jatropha palm biodiesel blends: an optimum mix for Asia. Fuels. 86: 1365-71.

Silitonga A, Masjuki H, Mahila T, Ong H, Chong W and Boosroh M (2013) Overview properties of biodiesel blends from edible and non-edible feedstocks. Renewable and Sustainable Energy Reviews. 22: 346- 360.

Sinha S, Agarwal A K and Garg S (2007) Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. Energy Conservation and Managment. 49: 1248-1257.

Starvarache C, Vinatoru M, Nisimura R and Maeda Y (2005) Fatty acids methyl esters from vegetable oils by means of ultrasonic energy. Ultrasonics Sonochemistry. 12: 367-372.

Tang Y, Meng M, Zhang J and Lu Y (2011) Efficient preparation of biodiesel from rapeseed oil over modified CaO. Applied Energy. 88: 2735-2739.

Veljkovic V B, Avramivic J M, Stamenkovic O S (2012) Biodiesel production by ultrasound-assisted transesterification: State of the art and the perspectives. Renewable and Sustainable Energy Reviews. 16: 1193–209.

Wikipedia “https://en.wikipedia.org/wiki/Jatropha_curcas” Accessed on 19 March 2015.

Xin J, Imahara H and Saka S (2008) Oxidation stability of biodiesel fuel as prepared by supercritical methanol. Fuels. 87:1807-13.

Zanette A F, Barella R A, Pergher S B C, Treichel H, Oliveira D, Mazutti M A, Silva E A and Oliveira J V (2011) Screening, optimization and kinetics of Jatropha curcas oil transesterification with heterogeneous catalysts. Renewable Energy. 36: 726-731.

Zanuttini M S, Pisarello M L and Querini C A (2014) Butia Yatay coconut oil: Process development for biodiesel production and kinetics of esterification with ethanol. Energy Conservation and Managment. 85: 407-416.

Zhang Y, Li Y, Zhang X and Tan T (2015) Biodiesel production by direct transesterification of microalgal biomass with co-solvent. Bioresource Technology. 196: 712-715.

Zhou D, Qi L, Qiao B Q, Xu Q Q and Yin J Z (2017) Continuous production of biodiesel from soybean flakes by extraction coupling with transesterification under supercritical conditions. The Journal of Supercritical Fluids. 120(2): 395-402.