

**KUMARAGURU COLLEGE OF TECHNOLOGY  
COIMBATORE - 641 049**

DEPARTMENT OF BIOTECHNOLOGY

**PROJECT WORK  
PHASE II  
APRIL 2012**

This is to certify that the project entitled  
**BIODIESEL PRODUCTION FROM  
OIL SEEDS OF *Simarouba glauca***  
is the bonafide record of project work done by

**SELVAKUMAR S  
Register No: 1020203014**

of M.Tech (Biotechnology) during the year 2011-2012

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Project Guide .....  
Head of the Department

Submitted for the project Viva-Voce examination held on.....

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Internal Examiner .....  
External Examiner

**BIODIESEL PRODUCTION FROM  
OIL SEEDS OF *Simarouba glauca***



**PROJECT REPORT  
Submitted by**

**SELVAKUMAR S  
Register No: 1020203014**

*in partial fulfilment for the award of the degree*

*of*

**MASTER OF TECHNOLOGY**

**IN**

**BIOTECHNOLOGY**

**KUMARAGURU COLLEGE OF TECHNOLOGY**  
(An Autonomous Institution Affiliated to Anna University of Technology, Coimbatore)  
COIMBATORE -641 049

APRIL 2012

**DECLARATION**

I affirm that the project work titled "**BIODIESEL PRODUCTION FROM OIL SEEDS OF *Simarouba glauca***" being submitted in partial fulfilment for the award of M.Tech (Biotechnology) is the original work carried out by me. It has not formed the part of any other project work submitted for award of any degree or diploma, either in this or any other university.

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## ABSTRACT

Transesterification reaction was carried out using simarouba oil as an oil source for making biodiesel. In this three different variables such as reaction temperature, oil to alcohol ratio and reaction time were studied. Formation of methyl esters due to reduction of free fatty acids are observed in GC – MS analysis. In the present study the optimum conditions for better yield of biodiesel are oil to alcohol ratio 3, temperature 75°C, time 23 h produce a FFA 0.07. The fuel properties of simarouba oil fulfil the requirements of Indian standards for biodiesel. Then simarouba oil was blended with palm oil at various concentrations. In that 33:11 ratio of simarouba oil and palm oil gives better yield of 82% of biodiesel recovery.

**Key words:** Transesterification, simarouba, biodiesel, methyl esters

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## LIST OF ABBREVIATIONS

°C	Degree Centigrade
ANN – GA	A Genetic Algorithm Coupled with Artificial Neural Network
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
B100	100% Biodiesel
B20	20% Biodiesel
B5	5% Biodiesel
BAP	Benzyl Adenaine Purine
BF <sub>3</sub>	Boron trifluoride
BP	Brake Power
BTh	Brake Thermal efficiency
C – PER	Computed Protein Efficiency Ratio
C.I Engine	Compression Ignition Engine
CaO	Calcium Oxide
CO	Carbon monoxide
CO <sub>2</sub>	Carbon di oxide
CO <sub>x</sub>	Carbon monoxide
D.I engine	Direct Ignition engine
EAAI	Essential Amino Acid Index
eGFP	Efficient Gene Fluorescence Protein
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acids
GC	Gas Chromatography
GFP	Gene Fluorescence Protein
GUS	β - Gluturonidase
h	Hour
H <sub>2</sub> SO <sub>4</sub>	Sulphuric Acid
H <sub>3</sub> PO <sub>4</sub>	Phosphoric Acid
HC	Hydro Carbon

HCl	Hydrochloric Acid
Hg	Mercury
HPLC	High Performance Liquid Chromatography
IBA	Indole 3- Butyric Acid
JCO	<i>Jatropha curcas</i> Oil
JTC	<i>Jatropha curcas</i>
kDa	Kilo Dalton
kg	Kilogram
KOH	Potassium Hydroxide
M	Methanol to oil ratio
m	Meter
ME	Methyl Ester
Me50-Eu50	50% Methyl Esters of Paradise oil and 50% Methyl Esters of Eucalyptus Oil
MEPS	Methyl Esters of Paradise oil
mg	Milligram
mm	Millimeter
MMT	Million Metric Ton
Mol	Mole
MS	Murashige Skoog
NaOH	Sodium Hydroxide
NO <sub>x</sub>	Oxides of Nitrogen
OAR	Oil Alcohol Ratio
OH	Hydroxyl ion
OLL	Oleic – Linoleic – Linoleic Acid
OOL	Oleic – Oleic – Linoleic Acid
Pb	Lead
PDCAAS	Protien Digestability Corrected Amino Acid Score
PKBS	<i>Parkia biglobbossa</i>
Psi	Pounds per square inch
RBO	Rice Bran Oil
Rpm	Roles per minute
RSM	Response Surface Methodology

SDS – PAGE	Sodium Dodecyl Sulphate – Polyacrylamide Gel Electrophoresis
Sn	Tin
SOME	Simarouba Oil Methyl Ester
Std	Standard
T	Temperature
t	Time
TAG	Tri Acyl Glycerides
TDZ	Thiadazuron
TEMP	Temperature
TFC	Total Fuel Consumption
THF	Tetra Hydro Furan
TLC	Thin Layer Chromatography
v/v	Volume per volume
w/w	Weight per Weight
wt	Weight
yr	Year
Zn	Zinc

## CHAPTER 1

### INTRODUCTION

#### 1.1 GENERAL

Self-reliance in energy is vital for overall economic development of India and other developing countries in the world. The need to search for alternative sources of energy which are renewable, safe and non polluting assumes top priority in view that fossil fuel sources are finite, are the major source of releasing sequestered carbon to atmosphere as CO<sub>2</sub> and CO causing global warming. In addition, uncertain supplies and frequent price hikes of fossil fuels in the international market are posing serious economic threats for developing countries (Wani and Sreedevi, 2005).

In the Indian context, the estimated import of crude oil may go up from 85 to 147 MMT per annum by the end of 2006-2007, correspondingly increasing the import bill from \$13.3 to \$15.7 billion (Biofuel Report, 2003). Hence, efforts are being made to explore for alternative source of energy. Biodiesel, an alternative fuel, must be technically feasible, economically competitive, environmentally acceptable and readily available (Srivastava and Prasad, 2000).

Chemical transesterification or alcoholysis of triglycerides or the esterification of free fatty acids using short-chain alcohols in the production of alkyl esters or biodiesel was first reported on August 31<sup>st</sup> 1937 in a Belgian Patent by Chavanne of the University of Brussels (Knothe, 2001). In the early 1940s researches that did not actually anticipate the production of alkyl esters as fuel were patented (Chavan, 1937; Bradshaw, 1942; Bradshaw and Mealy 1942; Bradshaw and Meuly 1944; Arrow and Rose; Allen *et al.*, 1945; Walter 1945). A simplified method for extracting glycerol during soap production was reported (Van Garpen, 2005). The glycerol was needed for wartime explosives production. The glycerol could be separated since it is insoluble in the esters and has a much higher density that makes settling or centrifugation a choice process in its removal.

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biodiesel production.

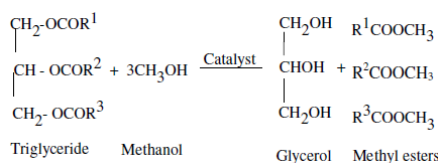


Figure 1.1: Transesterification of triglycerides

#### 1.2 CATALYST SYSTEMS USED IN BIODIESEL PRODUCTION

##### 1.2.1 Base-catalyzed processes

Several conventional and non-conventional base-catalyzed transesterification processes have been reported in a review by Knothe *et al.*, 1997. Boiler ashes, potassium hydroxide (KOH) amongst other catalysts were successfully used in the ethanolysis and methanolysis of palm and coconut oils with yields as high as 90% (Graille *et al.*, 1986; Encinar *et al.*, 2002; Ejikeme *et al.*, 2008; Ejikeme 2007; Ejikeme *et al.*, 2008). It has also been reported that methyl and ethyl esters with 90% yield can be obtained from palm and coconut oil from the press cake and oil mill and refinery waste with the ashes of the wastes (fibers, shell, and husks) of these two oil seeds, and with lime, clay, zeolites, etc (Graille *et al.*, 1982; Sasidharan and Kumar, 2004; Bandger *et al.*, 2001; Ponde *et al.*, 1998). Methanolysis has been reported to yield 96-98% esters when palm oil is refluxed for 2 h. Using coconut-shell ash and other ashes from the combustion of plant wastes such as fibres of palm tree that contain potassium and sodium carbonate (Graille *et al.*, 1985). Calcium oxide on magnesium oxide has been shown, at 60-63°C, to be the best catalyst system amongst potassium carbonate, sodium carbonate, iron (III) oxide, sodium methoxide, sodium aluminate, zinc, copper, tin, lead and zinc oxide in the methanol transesterification of low-erucic rapeseed oil (Peterson and Scarrah, 1984).

Generally, the mechanism of the base-catalysed transesterification of vegetable oils involves four steps. The first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The second step is the nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generating a tetrahedral intermediate (Taft *et al.*, 1947; Guthrie, 1991; Meher *et al.*, 2006). The third step involves the formation of the

Transesterification reaction of vegetable oils can be represented as in Figure 1.1. The reaction does not proceed to any appreciable extent in the absence of catalysts or supercritical condition. Various homogeneous and heterogeneous catalysts, ranging from base, acid to enzyme (Freedman and Pryde, 1982; Komers *et al.*, 2001), have been developed for use in

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alkyl ester and the corresponding anion of diglyceride. The final step involves deprotonating the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol. The above steps are summarized in Figure 1.2.

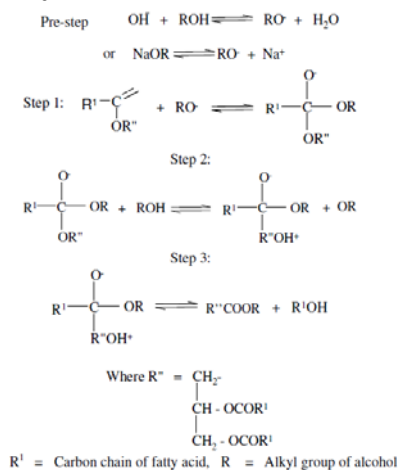


Figure 1.2: The mechanism of base-catalyzed transesterification of vegetable oils

The base-catalyzed transesterification of vegetable oils are reported to proceed faster than the acid-catalyzed reactions (Freedman *et al.*, 1986). Because of this and the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favour base catalysts, such as alkaline metal alkoxides (Schwab, 1987) and hydroxides (Aksoy *et al.*, 1990; Gryglewicz, 2000; Albis Arrieta *et al.*, 2005) as well as sodium or potassium carbonates (Graille *et al.*, 1985; Hirano *et al.*, 2000). Alkaline metal alkoxides (as CH<sub>3</sub>OM for the methanolysis) are the most active catalysts. They give yields greater 98% in a relatively short reaction time of 30 min even at low molar concentrations of about 0.5 mol(%) , but their requirement of the absence of water makes them inappropriate for typical

industrial processes in which water cannot be avoided completely (Freedman and Pryde, 1984).

Alkaline metal hydroxides (e.g. KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol(%). However, even if water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide and the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester (Figure 1.3), with consequent soap formation (Freedman and Pryde, 1984). In 2003, metal complexes of the type M (3-hydroxy-2-methyl-4-pyrone)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, where M = Tin (Sn), Zinc (Zn), Lead (Pb) and Mercury (Hg) were used for soybean oil methanolysis under homogeneous conditions (Abreu *et al.*, 2003). The Sn complex at a molar ratio of 400:100:1 methanol:oil:catalyst gave 90% conversion in 3 h, while the Zn complex gave only 40% conversion under the same conditions. This undesirable saponification reaction reduces the ester yields and considerably makes difficult the recovery of the glycerol due to the formation of emulsions, increase in viscosity and greatly increased product separation cost.

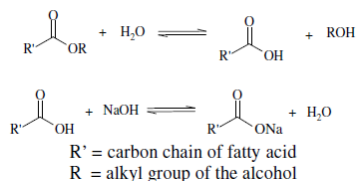


Figure 1.3: Hydrolysis of esters and formation of soap by the presence of water

Potassium carbonate, used in a concentration of 2 or 3 mol% gives high yields of fatty acid alkyl esters and reduces the soap formation (Filip *et al.*, 1992). This can be explained by the formation of bicarbonate instead of water (Figure 1.4), which does not hydrolyze the esters. There are other heterogeneous base catalysts which have been tested with promising results (Kim *et al.*, 2004; Gryglyewicz, 1999). Also, solid bimetallic catalysts like Sn-Ni (Uresta *et al.*, 2000), exchange resins, zeolites (Leclereq *et al.*, 2001; Reis *et al.*, 2003), organometallic compounds (Gheorghiu, 1996) and mixed oxides (Monteriro and Cruz, 2004;

Stoffel *et al.*, 1959). Carboxylic acids can be formed by reaction of the carbocation with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids, which reduce the yield of alkyl esters.

The transesterification process in biodiesel production is catalyzed by Bronsted acids like HCl, BF<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and sulphonic acids (Stern *et al.*, 1990; Formo, 1954). Preferably, sulphonic and sulphuric acids are mostly used. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring typically, temperatures above 100°C and from 3-48 h to reach complete conversion (Zheng *et al.*, 2006; Zhang *et al.*, 2003; Jeromin *et al.*, 1987; Guan *et al.*, 2009; Nye, 1983; Harrington and Arcy-Evans, 1985). The methanolysis of soybean oil, in the presence of 1 mol% of H<sub>2</sub>SO<sub>4</sub>, with an alcohol/oil molar ratio of 30:1 at 65°C, takes 50h to reach complete conversion of the vegetable oil (>99%), while the butanolysis (at 117°C) and ethanolysis (at 78°C) using the same quantities of catalyst and alcohol take 3 h and 18 h, respectively (Freedman *et al.*, 1986).

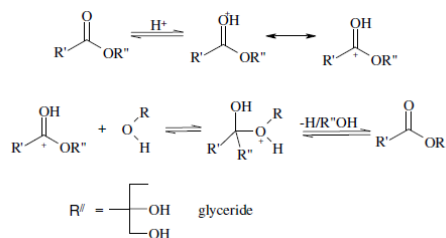


Figure 1.5: A typical mechanism of acid catalyzed transesterification of vegetable oils.

Reaction rates in acid-catalyzed processes may be increased by the use of larger amounts of catalyst. Typically, catalyst concentrations in the reaction mixture have ranged between 1 and 5 wt % in most academic studies using sulphuric acid (Freedman *et al.*, 1986). The different concentrations of sulphuric acid (1, 3 and 5 wt %) were used in the transesterification of grease with methanol (Canakci and Van Garpen, 1999). In these studies,

Bourmaya *et al.*, 2005; Stern *et al.*, 1999) have been developed and used in transesterification reactions.

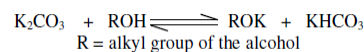


Figure 1.4: Equation of reaction for bicarbonate formation

In addition, P(RNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N (Iankumaran and Verkade, 1999), multifunctionalized (Mbaraka and Shanks, 2005) as well as organosulphonic acid functionalized mesoporous silicas (Mbaraka *et al.*, 2003), all of which for industrial applications require high temperature and pressure are available. The base-catalyzed reaction is most often used because:

- ❖ It uses low temperature (60°C) and pressure (20 psi) processing.
- ❖ It achieves high conversion (98%) with minimal side reactions and low reaction time.
- ❖ Conversion to methyl ester is direct with no intermediate steps.

Base-catalyzed transesterification of vegetable oils results in good yields of the esters (Stoffel *et al.*, 1959). Nevertheless, there are obvious problems encountered by their use. Some of these problems have been identified to include:

- ❖ Post-reaction treatment of the alkaline waste-water to obviate the environmental effects of its disposal
- ❖ High energy demand
- ❖ Post-reaction treatment to remove the catalyst from the product-biodiesel
- ❖ Interferences occasioned by the presence of free fatty acid and water during the reaction and
- ❖ Difficulty in the recovery of glycerol after the reaction

The development of acid and heterogeneous catalyst systems, some of which run in continuous reactors, have addressed many of these problems which ordinarily meant higher production costs and less economic viability relative to petroleum-based diesel.

### 1.2.2 Acid-catalyzed processes

The mechanism of the acid-catalyzed transesterification of vegetable oils is as shown in Figure 1.5 for a monoglyceride. The protonation of the carbonyl group of the ester leads to the carbocation which after a nucleophilic attack of the alcohol produces the tetrahedral intermediate. This in turn eliminates glycerol to form the new ester, and to regenerate the

a rate enhancement was observed with the increased amounts of catalyst and ester yield increased from 72.7 to 95.0% as the catalyst concentration was increased from 1 to 5 wt%. The dependence of reaction rate on catalyst concentration has been further verified by the same authors and other groups (Canakci and Van Garpen, 2001a; Crabba *et al.*, 2001). A further complication of working with high acid catalyst concentration becomes apparent during the catalyst neutralization process, which precedes product separation. Since CaO addition during neutralization is proportional to the concentration of acid needed in the reactor, high acid concentration leads to increased CaO cost, greater waste formation, and higher production cost.

### 1.2.3 Enzyme-catalyzed processes

Due to their ready availability and the ease with which they can be handled, hydrolytic enzymes have been widely applied in organic synthesis. They do not require any coenzymes, are reasonably stable, and often tolerate organic solvent (Siakpas *et al.*, 2006). Their potential for regioselective and especially for enantioselective synthesis makes them valuable tools (Shimada *et al.*, 2001). Immobilized *Candida Antarctica* lipase has been used for ethyl esterification of docosahexanoic acid (Shimada *et al.*, 2001) and latter used to effect over 98.5% fatty acid methyl ester conversion (Hsu *et al.*, 2002; Watanabe *et al.*, 2005).

Although the enzyme-catalyzed transesterification processes are not yet commercially developed, new results have been reported in recent articles and patents (Posorske, 1984). A solution to the inhibition of enzyme activity by high concentration of methanol as well as water generated during the reaction have been proffered by many authors (Hsu *et al.*, 2002; Belafi-bako *et al.*, 2002; Shimada *et al.*, 2002; Watanabe *et al.*, 2002) to include carrying out the reaction with immobilized enzymes and the use of multiple stages. The common aspects of these studies consist in optimizing the reaction conditions (solvent, temperature, pH, type of microorganism which generates the enzyme, etc.) in order to establish suitable characteristics for an industrial application. However, the reaction yields as well as the reaction times are still unfavourable compared to the base-catalyzed reaction systems, though Shimada and co-workers reported that the stepwise addition of methanol gave 98% conversion of oil to methyl ester with an amazing re-use of the immobilized enzyme for 50 times (Posorske, 1984). Several reports exist on lipase catalyzed transesterification process with extracellular and intracellular lipases as catalyst in either aqueous or non-aqueous

systems (Belafi-bako *et al.*, 2002; Shimada *et al.*, 2002; Watanabe *et al.*, 2002; Shimada *et al.*, 1999; Du *et al.*, 2003; Nelson *et al.*, 1996).

The incubation of *Candida antarctica* lipase consecutively in methyl ester (oleate) for 30 min and in soybean oil for 12 h has been reported to lead to a dramatic increase in the efficiency of the enzyme, giving almost 100% conversion (Samukawa *et al.*, 2000). Lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors, others (Du *et al.*, 2004; Scragg *et al.*, 2003; Karl-Erich and Thorsten, 2002; Vanessa and Park, 2004), reported the use of other enzymes like *Chlorella vulgaris* and *Candida cylindracea* in the conversion of other oils to biodiesel.

### 1.3 POTENTIAL OIL SOURCES

#### 1.3.1 Jatropha

Kingdom: Plantae  
Order: Malpighiales  
Family: Euphorbiaceae  
Genus: *Jatropha*  
Species: *Curcas*

*Jatropha curcas* L. (Family Euphorbiaceae) has assumed paramount importance as a potential biodiesel crop in more than 50 countries. It is a plant with several attributes, multiple uses and considerable potential (Heller, 1996). *Jatropha curcas* (Linnaeus) is a multipurpose small tree or shrub belonging to the family of Euphorbiaceae. It is a native of tropical America, but now thrives in many parts of the tropics and sub-tropics in Africa and Asia. *J. curcas* the new cultivated and promising crop is convenient to adapt in Egypt for increasing the local planted production (MSEA, 2008). In Egypt, the primary use of *J. curcas* seeds is for oil extraction which is a good alternative to biofuel, and has proven a success when used either independently or by mixing the diesel to operate farm machinery, household lighting, in soap and candles (El-Gamassy, 2008).

All parts of the plant-roots, stems, leaves seeds and fruits-have been widely used in traditional folk medicine in many parts of West Africa (Adamu *et al.*, 2006) and used for veterinary purposes for a long time (Duke, 1985). *J. curcas* and their extracts are used in traditional medicine, e.g. antimicrobial (Thomas, 1989; Ravindranath *et al.*, 2004), antiviral

Historically, this plant has been used in India and neighbouring regions as a source of traditional medicines, animal fodder, green manure, timber, fish poison and fuel. More importantly, *P. pinnata* has recently been recognized as a viable source of oil for the burgeoning biofuel industry. The sustainable production of plant oils for biodiesel production from a tree crop such as *P. pinnata*, which can be cultivated on marginal land, has the potential to not only provide a renewable energy resource but in addition will alleviate the competitive situation that exists with food crops as biofuels and associated arable land and water use.

*P. pinnata* is a nitrogen-fixing tree and therefore a member of the family Leguminosae. More detailed taxonomic description places it in the subfamily Papilionoideae and the tribe Millettieae. This plant has been synonymously known as *P. pinnata* Merr., *Pongamia glabra* Vent., *Derris indica* (Lam) Bennett and *Milletia novo-guineensis* Kane & Hat.

#### 1.3.3 Simarouba

Kingdom: Plantae  
Order: Sapindales  
Family: Simaroubaceae  
Genus: *Simarouba*  
Species: *glauca*  
Binomial name *Simarouba glauca*

*Simarouba glauca*, D.C. (Simaroubaceae), which is native to Central America and popularly known as aceituno, was introduced to India in the early 1960s. It is an evergreen tree with profuse deep green, glossy foliage on its rounded crown and has the habit of growing sprawling branches from almost the ground level in its early stages of growth. The plant begins fruiting at about 5 – 6 yr of age and yields for up to 50 – 60 yr. A mature plant yields about 20 – 50 kg of brown-coloured oval-shaped seeds (Pradhan *et al.*). It has been reported that the seeds contain 40% kernels and the kernels contain 60% fat, which is edible. The odourless, greenish-yellow fat melts at 26.4°C, has an iodine value of 52.6, and a saponification value of 190.5. The average values of major fatty acids reported were: oleic (51.1%), stearic (30.4%), and palmitic (12.6%) (Coleman *et al.*, Chikara *et al.*, Severan *et al.*, Rao *et al.*, Rath *et al.*). Further, it has been reported that the characteristics of the fat and the

(Matsuse *et al.*, 1998), acaricidal activity (Dimri and Sharma 2004), insecticidal properties (Jing *et al.*, 2005; Georges, 2008), coagulant and anticoagulant activities (Osoniyi and Onajobi 2003), antimolluscicidal (Yasuraoka *et al.*, 1980; Liu *et al.*, 1997; Rug and Ruppel 2000) and anti-inflammatory (Mujumdar and Misra 2004).

*Jatropha curcas* L. is a perennial deciduous, multipurpose shrub belonging to the family Euphorbiaceae, native to Central America region and later distributed in many parts of the tropic and subtropic regions of the world. Primarily *J. curcas* plant was used for its medicinal values, however, recently received tremendous attention for its seed oil that can be converted into biodiesel and is considered to be a universally acceptable as an energy crop and alternative to conventional fossil fuels (Takeda, 1982).

#### 1.3.2 Pongamia

Kingdom: Plantae  
Order: Fabales  
Family: Fabaceae  
Genus: *Pongamia*  
Species: *Pinnata*

*Pongamia pinnata* popularly known as 'Karanj' or 'Karanja' is commercially important tree species used to produce biofuels that can grow on waste land or unproductive land. The tree is adaptable to wide agro climatic conditions. Besides the oil-yielding capacity, its multipurpose benefits as a provider of green manure and medicine and its role in agro-forestry make it a potential candidate for large-scale plantation on marginal lands. It is recommended as a shade tree for pastures and a windbreak for tea (Duke, 1983). It can also play a role in rural economy by generating huge manpower employment during various stages of its cultivation as well as during downstream processing (Shrinivasa, 2001). However, while utilizing these species as a source of biodiesel, there is a further need for research into various areas of production (Kesari *et al.*, 2008).

*Pongamia pinnata*, an arboreal legume, is a member of the subfamily Papilionoideae, more specifically the Millettieae tribe. This medium-size tree is indigenous to the Indian subcontinent and south-east Asia, and has been successfully introduced to humid tropical regions of the world as well as parts of Australia, New Zealand, China and the USA.

fatty acid composition of Indian origin do not significantly differ from those reported from seeds of other countries. (Rao *et al.*, Rath *et al.*)

Simarouba (*Simarouba glauca* L.) commonly known as aceituno, paradise-tree or bitter wood is a medium sized evergreen tree (height 7 - 15m). It grows well up to 1000 m above sea level in all types of well drained soils (pH 5.5 to 8.0) and has been found to be established in places with 250 mm to 2500 mm annual rainfall and temperatures going up to 45°C (Joshi and Hiremath, 2001). Simarouba tree is found in dry areas. As it withstands dry and semi arid conditions, it can be planted in areas where no other plants of economic value can be grown. In a hectare of land about 200 trees can be accommodated. It produces fruits similar in size, shape and colour to olives. There are two varieties; one produces greenish white fruit and other violet to almost black fruits (Reddy *et al.*, 2003). The tree begins to produce fruit at about four years of age but it comes to full production at six years of age. The tree starts flowering during December and bear fruits in January and February. The fruit lets are ready to harvest in May. Though the tree commences bearing fruit from fourth year of planting, economic yields of about 20 kg fruits per tree can be harvested only from the 10<sup>th</sup> year of planting. The average yield of fruit from a hectare from a 10-year-old plantation of Simarouba will be about 6,000 to 8,000 kg (Joshi and Hiremath, 2001).

### 1.4 TRANSESTERIFICATION

Ethyl ester reacts with methanol to form a methyl ester and ethanol. This process is called transesterification. Transesterification is extremely important for biodiesel. Biodiesel as it is defined today is obtained by transesterifying the triglycerides with methanol. Methanol is the preferred alcohol for obtaining biodiesel because it is the cheapest alcohol. However, for the reaction to occur in a reasonable time, methanol is added as a catalyst to the mixture of the vegetable oil and methanol. The alcohol used for producing biodiesel is usually methanol.

For the transesterification to occur, usually 6 moles of alcohol are used for every mole of triglyceride, which is more than the stoichiometric equation indicates. The reason is that the reaction is desired to proceed in the direction to the right. In other terms, the equilibrium of the reaction needs to be shifted toward the right side of the equation. As the term equilibrium indicates, not all reactions easily proceed to completion and after some time the

starting materials and reaction products are present in constant amounts (the equilibrium has been attained).

In many cases, the fact that a reaction can proceed in the reverse fashion (from right to left in the equation) also plays a role in formation of the equilibrium. To force the equilibrium in the direction of the products (as is almost always desired), one or more parameter(s) of the reaction may need to be changed. Such parameters include the molar ratio as well as others such as temperature, pressure and use of a catalyst.

In accordance with the names of fatty acids and their esters, the methyl ester of Simarouba oil is called Simarouba oil methyl ester (SOME) is also very common. Another common abbreviation that is commonly used is FAME (fatty acid methyl ester). Besides triglycerides, mono- and diglycerides can also exist. They are formed as intermediates during the transesterification reaction. This is one of the problems when conducting chemical reactions in general, not only the transesterification reaction. It is almost always the goal of chemical reactions to obtain products that are as pure as possible. However, hardly any chemical reaction proceeds to full completion. Therefore, often intermediates (in the case of transesterification the intermediates are partially reacted triglycerides, i.e., the mono- and diglycerides) can contaminate the final product. Other materials that can contaminate biodiesel are residual methanol (or other alcohol), glycerol, and catalyst.

When the transesterification reaction is conducted, not all materials can be readily mixed with each other. A term often used for this phenomenon is that there are two phases. At the start of the reaction, methanol and vegetable oil do not readily mix. At the end of the reaction, there are two layers (phases), one consisting mainly of glycerol, the other of the methyl esters. Obviously, glycerol and methyl esters do not mix readily. How readily one compound will dissolve in another depends on the structural features of the compounds, for example the existence of OH groups. Thus, compounds containing OH groups and those not containing OH groups often will not readily mix.

Xiaohu *et al.* (2009) evaluated the feasibility of using recycled canola oil as raw material to produce ASTM standard biodiesel. Two-step reaction, acid-catalyzed esterification followed by alkali-catalyzed transesterification, was performed. The high level of free fatty acids (FFA) in the recycled canola oil was reduced to less than 1% by acid catalyzed esterification with 40:1 molar ratio of methanol to FFA in the presence of 5% (v/v, based on FFA) sulphuric acid. Further alkali-catalyzed transesterification was carried out at 6:1 molar ratio of methanol to oil and 1% (wt%, based on oil weight) potassium hydroxide. The characterization of produced biodiesel showed that it met the ASTM D 6751 with respect to the kinematic viscosity at 40°C, acid number, flash point, water and sediment, cold soak filtration test, oxidation stability, free and total glycerin etc. At the same time, the properties of by-product crude glycerol, such as flash point, moisture by Karl Fisher, ash, glycerol content, were also characterized, which can facilitate further glycerol purification and expand its applications, thus enhancing the overall profitability of the biodiesel production process.

Haq *et al.* (2008) focused on the acid and base catalyzed transesterification of animal fats to produce biodiesel by varying process parameters such as catalyst amount, catalyst nature, reaction time and temperature. The maximum biodiesel yield after acid catalysis was  $94.1 \pm 2.43$  and  $98.4 \pm 2.3$  percent for dairy cow and beef tallow, respectively. The quantity of biodiesel obtained after base catalysis was comparatively lower than obtained in case of the acid catalysis. The optimum conditions for biodiesel production using acid catalysis were: 2.5 g of conc.  $H_2SO_4$ , 24 h of reaction time and 50°C for dairy cow fat and 2.5 g of conc.  $H_2SO_4$ , 6 h of reaction time and 60°C for beef tallow. The amount of biodiesel obtained from beef tallow in the present study was much higher than earlier reported yields. The evaluation of transesterification process was followed by gas chromatographic analysis of tallow fatty acid esters (biodiesel) at optimal conditions. The fuel properties of biodiesel thus obtained accomplished the requirements of both the American and European standards for biodiesel.

Mushatq *et al.* (2010) investigated sunflower oil for biodiesel production. Sunflower is one of the leading oil seed crop, cultivated for the production of oil in the world. It has also been considered as an important crop for biodiesel production. Seeds for biodiesel production were procured from local farmers of Attock and Rawalpindi divisions. Electric oil expeller was used for the extraction of crude oil. Base catalyzed transesterification process is applied for optimum yield (80%) of biodiesel. Fuel properties of sunflower oil biodiesel were compared with American Society for Testing and Materials (ASTM). Engine efficiency of

## CHAPTER 2 LITERATURE REVIEW

### 2.1 GENERAL

Karmakar *et al.* (2010) reviewed physicochemical properties of the plant and animal resources that are being used as feedstock for biodiesel production. As an alternative fuel, biodiesel is becoming increasingly important due to diminishing petroleum reserves and adverse environmental consequences of exhaust gases from petroleum-fuelled engines. Biodiesel, the non-toxic fuel, is mono alkyl esters of long chain fatty acids derived from renewable feedstock like vegetable oils, animal fats and residual oils. Choice of feedstock depends on process chemistry, physical and chemical characteristics of virgin or used oils and economy of the process. Extensive research information is available on transesterification, the production technology and process optimization for various biomaterials. Consistent supply of feedstock is being faced as a major challenge by the biodiesel production industry. Efforts have also been made to review the potential resources that can be transformed into biodiesel successfully for meeting the ever increasing demand of biodiesel production.

Srivathsan *et al.* (2008) analyzed biodiesel production methods reported in literature and also suggest a suitable method for commercialization of the enzymatic process. Biodiesel production has received considerable attention in the recent past as a biodegradable and non-polluting fuel. The production of biodiesel by transesterification process employing alkali catalyst has been industrially accepted for its high conversion and reaction rates. Recently, enzymatic transesterification has attracted much attention for biodiesel production as it produces high purity product and enables easy separation from the byproduct, glycerol. But the cost of enzyme remains a barrier for its industrial implementation. In order to increase the cost effectiveness of the process, the enzyme (both intracellular and extracellular) is reused by immobilizing in a suitable biomass support particle and that has resulted in considerable increase in efficiency. But the activity of immobilized enzyme is inhibited by methanol and glycerol which are present in the reacting mixture. The use of t-butanol as solvent, continuous removal of glycerol, stepwise addition of methanol are found to reduce the inhibitory effects thereby increasing the cost effectiveness of the process.

biodiesel with reference to power, efficiency and consumption of biodiesel blends (B100, B20 and B5) were determined. It was concluded that sunflower oil is one of the option for biodiesel production at a large scale depending on its mass cultivation.

Savita *et al.* (2010) estimated primary metabolites such as sugar, starch, protein, lipid, phenol, ascorbic acid and amino acid which are present in different plant parts of *Pongamia pinnata*. The highest amount of starch (81.90mg/gdw), protein (24.0mg/gdw) and ascorbic acid (3.02mg/gdw) was observed in roots, soluble sugar (45.0mg/gdw), phenol (0.76mg/gdw), and amino acids (10.0mg/gdw) in leaves, lipids (358mg/gdw) in seeds. Similarly lowest amount of phenol (0.20mg/gdw) was observed in roots, sugar (14.0mg/gdw) and ascorbic acid (1.06mg/gdw) in stems, starch (16.20mg/gdw), lipid (58.0mg/gdw) and protein (4.20mg/gdw) in leaves, amino acid (2.80mg/gdw) in seeds.

Emil *et al.* (2009) extracted and analyzed the lipid fraction of *Jatropha* oil seed for their chemical and physical properties such as acid value, percentage free fatty acids (%FFA), iodine value, peroxide value and saponification value as well as viscosity, and density. Due to the environmental concern and limited resources of petroleum oil has been increased the demand of biodiesel. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as non edible oils, animal fats, waste food oil and by products of the refining vegetables oils. The fact that *Jatropha* oil cannot be used for nutritional purposes without detoxification makes its use as energy/fuel source very attractive. The fatty acid and triacylglycerol (TAGs) composition of the extracted lipid was revealed using the gas chromatography (GC) and high pressure liquid chromatography (HPLC) method. Both oleic acid (44.7%) and linoleic acid (32.8%) were detected as the dominant fatty acids while palmitic acid and stearic acid were the saturated fatty acids found in the *Jatropha* oil. Characterisation and Composition of *Jatropha Curcas* oil seed from Malaysia was studied for its potential as biodiesel feedstock. OLL (22.94%) and OOL (17.9%) were detected as major triacylglycerol composition in the *Jatropha* oil. The oil extracts exhibited good physicochemical properties and could be useful as biodiesel feedstock and industrial application.

Akpan *et al.* (2011) carried out experimental study, through extraction and characterization of both crude and refined castor oil. Normal hexane was used as solvent for the extraction process. The oil produced was refined through degumming, neutralization and

bleaching process using local adsorbent (activated clay). The characterization analysis revealed that tested parameters, which include specific gravity, refractive index, acid value, saponification value and iodine value for both crude and refined castor oil produced, were within the ASTM standard specifications. In fact the iodine value obtained (84.8) for the refined oil indicates that the oil could certainly be used as lubricant, hydraulic break fluid and protecting coatings. The oil was modified via sulphation method to produce Turkey – red oil that was tested on wooden material, paper and cloth. The test revealed that the Turkey – red oil produced is suitable to be used as a good dyeing agent and polish.

Prabhakar *et al.* (2011 a) carried out an experiment to evaluate the sound, exhaust gas temperature and smoke opacity characteristics of a single cylinder, four stroke engine fuelled with vegetable oil methyl ester and its blends with standard diesel. Among different vegetable oils which can be used as alternate fuels, five vegetable oils, i.e., Nerium (*Nerium oleander*), *Jatropha* (*Jatropha curcas*), *Pongamia* (*Pongamia pinnata*), Mahua (*Madhuca indica*) and Neem (*Azadirachta indica*) oils were selected for analysis. Tests has been conducted using the fuel blends of 20%, 40%, 60% and 80% biodiesel with standard diesel, with an engine speed of 1800 rpm. It has found that the sound, exhaust gas temperature and smoke opacity characteristics of vegetable oil methyl ester and its diesel blends closely followed those of standard diesel.

Dilip (2009) found that existing diesel could be operated with upto 30% nahor biodiesel blend. Use of mixed biodiesel in a conventional diesel engine indicated the performance characteristics of mixed biodiesel operation are comparable to those with pure diesel operation. Significant improvement in engine performance and emission characteristic for biodiesel fuelled engine comparable to diesel fuelled engine and improvement in brake thermal efficiency, specific fuel consumption reduction and exhaust smoke opacity reduction has been observed for biodiesel.

Prabhakar and Annamalai (2011 b) selected five non-edible vegetable oils (Nerium, *Jatropha*, *Pongamia*, Mahua & Neem) as alternate fuels and performed comparison analysis of performance and emission of C.I engines. A comparative analysis was done for methyl esters of different oils in blends with diesel of different proportions. It was observed that a diesel engine runs successfully on a blend of 20% biodiesel and 80% diesel fuel without affecting engine performance. Methyl ester from nerium oil, with properties close to diesel,

biodiesel production. They also reviewed the biology, distribution and chemistry of selected non-edible oil seeds plants. As the world confronts a reported food shortage and rising fuel prices, scientists around the globe are scrambling to develop biofuel feedstock that would not divert food crops to energy. It is apparent that the demand for biodiesel is expected to increase in near future and although many edible oils might be the cheapest feedstock for biofuel production. But it may not be sustainable source to meet this increasing demand. This justifies the need to use non-edible oil seeds that can be the reliable sustainable feedstock for biofuel production. Furthermore, most of the non-edible seeds bearing trees have the potential of reclaiming wasteland and does not compete with food crop for limited growing regions. It thus becomes imperative to search for dedicated non-edible feedstock and their suitability for biodiesel production.

Pramanik (2003) investigated the high viscous of the *Jatropha curcas* oil which has been considered as a potential alternative fuel for the compression ignition (C.I.) engine. The blends of varying proportions of *Jatropha curcas* oil and diesel were prepared, analyzed and compared with diesel fuel. The effect of temperature on the viscosity of biodiesel and *Jatropha* oil was also studied. The performance of the engine using blends and *Jatropha* oil was evaluated in a single cylinder C.I. engine and compared with the performance obtained with diesel. Significant improvement in engine performance was observed compared to vegetable oil. The specific fuel consumption and the exhaust gas temperature were reduced due to decrease in viscosity of the vegetable oil. Acceptable thermal efficiencies of the engine were obtained with blends containing up to 50% volume of *Jatropha* oil. From the properties and engine test results it has been established that 40–50% of *Jatropha* oil can be substituted for diesel without any engine modification and preheating the blends.

Shashikant *et al.* (2006) demonstrated a central composite rotatable design to study the effect of methanol quantity, acid concentration and reaction time on the reduction of free fatty acids content of mahua oil during its pretreatment for making biodiesel. All the three variables significantly affected the acid value of the product, methanol being the most effective followed by reaction time and acid catalyst concentration. Using response surface methodology, a quadratic polynomial equation was obtained for acid value by multiple regression analysis. Verification experiments confirmed the validity of the predicted model. The optimum combinations for reducing the acid level of mahua oil to less than 1% after pretreatment was 0.32 v/v methanol-to-oil ratio, 1.24% v/v H<sub>2</sub>SO<sub>4</sub> catalyst and 1.26 h

showed better performance and emission characteristics, followed by esters of *Jatropha*, *Pongamia*, Mahua and Neem oils. Hence nerium blend can be used in existing diesel engines without compromising the engine performance.

Jain and Sharma (2010) reported the results of kinetics of two step acid-base catalysed transesterification process carried out at an optimum temperature of 65 °C and 50°C for esterification and transesterification respectively under the optimum methanol to oil ratio of 3:7 (v/v), catalyst concentration 1% (w/w) for H<sub>2</sub>SO<sub>4</sub> and NaOH. Out of various non edible oil resources, *Jatropha curcas* oil (JCO) is considered as future feedstock for biodiesel production in India. Limited work is reported on the kinetics of transesterification of high free fatty acids containing oil. The yield of methyl ester (ME) has been used to study the effect of different parameters. The results indicate that both esterification and transesterification are of first order with reaction rate constant of 0.0031 min<sup>-1</sup> and 0.008 min<sup>-1</sup> respectively. The maximum yield of 21.2% of ME during esterification and 90.1% from transesterification of pretreated JCO has been obtained.

Akintayo (2004) analysed *Parkia biglobbosa* (PKBS) and *Jatropha curcas* (JTC) seeds for their proximate composition. The oil seeds were analysed for fatty acid, lipid classes, sterols and physicochemical characteristics. Proximate analysis revealed that the percentage crude protein, crude fat and moisture in PKBS were 32.40%, 26.525% and 10.18% respectively and 24.60%, 47.25% and 5.54% in JTC. Campesterol, stigmasterol, b-sitosterol, D5-avenasterol and D7-stigmasterol were identified in the seed oils, but b-sitosterol was most abundant, constituting 71.9% in JTC and 39.5% in PKBS. JTC oil had 72.7% unsaturated fatty acids with oleic acid predominating, while PKBS had 62% unsaturated fatty acids with linoleic acid being the most abundant. Results of lipid classes showed triglyceride as the dominant lipid species in the seed oils. Physicochemical analysis of the seed oils showed that they could be classified as semi drying oils and that they could be found applicable in alkyl resin and soap manufacture.

Ashwani and Satyawati (2011) attempted to make an assessment of current energy scenario, potential of non-edible oil over edible oils, selected non-edible oil seeds as biodiesel feedstock, impact of biofuel on environment and future direction. Experimental analysis by different researchers on these non-edible oils showed their great potential as feedstock for

reaction time at 60°C. After the pretreatment of mahua oil, transesterification reaction was carried out with 0.25 v/v methanol-to-oil ratio (6:1 molar ratio) and 0.7% w/v KOH as an alkaline catalyst to produce biodiesel. The fuel properties of mahua biodiesel so obtained are compliant with the requirements of both the American and European standards for biodiesel.

Hanna *et al.* (2005) produced biodiesel, a fuel comprised of mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fat (or mixture thereof), by transesterification, with glycerol being produced as by-product. Worldwide, 1 billion ton of diesel fuel is consumed annually. The total feedstock available for biodiesel production is 115 million tons. This represents less than 12% of diesel fuel use. The opportunities for the future of biodiesel include improvements in the conversion technology, which appears promising and expanding the amount of available feedstock through various plans to increase oil yields or oil seed production.

Yi and Shaik (2005) investigated the dewaxing and degumming of rice bran oil by methanolysis. Rice bran is a by product of rice milling that contains 15-23% lipids and a significant amount of nutraceutical compounds. Due to the presence of active lipase in the bran and the lack of economical stabilization methods, most bran is used a livestock feed or boiler fuel and most rice bran oil (RBO) produced is not of edible grade. Thus RBO is relatively an inexpensive raw material production of proteins, carbohydrates, phytochemical and the isolation and purification of value added nutraceuticals generated during biodiesel (BD) production from RBO are attractive options to lower the cost of BD. Production of BD from RBO can be carried out either via in situ esterification, lipase catalysed esterification, acid catalysed or base catalysed reactions. A single step reaction for the conversion of RBO with high free fatty acid content into BD, via acid catalyzed, base-catalysed or lipase catalysed, fails to attain high conversion in reasonably short time. Pretreatment of crude RBO such as dewaxing/ degumming is a crucial step because of its efficient methanolysis. The fatty acid composition of dewaxed/degummed RBO is similar to that of other vegetable oils, which are used as feedstock. Various byproducts generated from the rice bran during the production of BD and their applications also addressed.

Naveen and Sharma *et al.* (2005) demonstrated that non edible oils like *Jatropha*, *Pongamia*, *Argemone*, Mahua, Castor, Sal etc can be used for the production of biodiesel.



*Jatropha curcas* has enormous potential for biodiesel production in India. *J. curcas* is a multipurpose plant with many attributes and considerable potential. It is a tropical plant that grows in low to high rainfall areas and can be used to reclaim land as a hedge and/or as a commercial crop. Thus, growing it could provide employment, improve the environment and enhance the quality of rural life.

Kumkar *et al.* (2005) studied that mahua oil methyl ester perform well compared to other esters on the basis of performance and emissions. Mahua oil methyl, ethyl, and butyl esters were prepared and studied in a four stroke, direct injection diesel engine for their performance and emissions. The engine tests showed high thermal efficiency in case of methyl ester compared to all other esters and diesel fuel. Different emissions such as carbon monoxide (COx), Oxides of nitrogen (NOx), Hydrocarbon (HC) is low for alkyl esters compared to diesel. Among alkyl esters except NOx all tail pipe emissions are lower in case of methyl esters compared to other esters. The ethyl esters shows lower NOx emission compared to other esters.

Kalam and Majsuki (2005) investigated the biodiesel production from palm oil, its properties and engine test results to evaluate its performance on diesel engine. The potential of palm diesel to be commercially used depends on its price comparison with diesel fuel and its status of reservation. Increasing cost and pollution effects of fossil diesel fuel can be resolved through producing vegetable oil based fuels such as palm diesel. And also they discussed Malaysian palm diesel as well as global biodiesel status, standardization of biodiesel and commercial price consideration and various engine test results on break power, combustion, emissions, engine wear and lubrication performance.

Henry (2005) stated that all countries have unused biomass resources. Some are waste with costs for disposal, but others are cultivated and collected. Because arable lands are not abundant and vary greatly in fertility, access to water, harvesting cost and transportation costs, the decisions about what biomass to collect and how to use it must be wise. It is naive to view biomass as the panacea for the coming energy crisis because there is not enough in practical locations and the costs involved in retrieving and refining it will be relatively high. Major thrusts for commercialization of biomass refining are imminent, and fuel ethanol, despite its enormous potential, market may not be the profitable product. Comparison of

eucalyptus oil are prepared on a volume basis and used as fuels in a single cylinder, four-stroke DI diesel engine, to study the performance and emission characteristics of these fuels. In the investigation a methyl ester derived from paradise oil is considered as an ignition improver. The results show a 49% reduction in smoke, 34.5% reduction in HC emissions and a 37% reduction in CO emissions for the Me50–Eu50 blend with a 2.7% increase in NOx emission at full load. There was a 2.4% increase in brake thermal efficiency for the Me50–Eu50 blend at full load. The combustion characteristics of Me50–Eu50 blend are comparable with those of diesel.

Devan and Mahalakshmi (2009c) conducted experiments to study the performance, emission and combustion characteristics of a DI diesel engine using poon oil-based fuels. In the present work, poon oil and poon oil methyl ester are tested as diesel fuels in Neat and blended forms. The blends were prepared with 20% poon oil and 40% poon oil methyl ester separately with standard diesel on a volume basis. The reductions in smoke, hydrocarbon and CO emissions were observed for poon oil methyl ester and its diesel blend along with increased NOx emission compared to those of standard diesel. However, a reduction in NOx emission and an increase in smoke, hydrocarbon and CO emissions were observed for Neat poon oil and its diesel blend compared to those of standard diesel. The 40% poon oil methyl ester blend showed a 2% increase in brake thermal efficiency compared to that of standard diesel, whereas other fuels tested showed a decreasing trend. From the combustion analysis it was found that ignition delay was shorter for all fuels tested compared to that of standard diesel. The combustion characteristics of poon oil methyl ester and its diesel blend closely followed those of standard diesel.

Pradhan *et al.* (2009) investigated some physical properties of tree borne oil seed like *Jatropha*, *Karanja* and *Simarouba* fruit and kernel. The ever growing demand of energy and its consistent impact on the import bill for fossil fuel has necessitated the search for alternative and complementary sources of energy. Biodiesel, an alternative fuel, is gaining world wide acceptance as a solution to environmental problems, energy security, reducing imports and improving agricultural economy. India is a net importer of edible oil, hence the emphasis is on non-edible oils from plants such as *Jatropha*, *Karanja*, *Simarouba*, etc. which could be utilized as a source for production of oil. Physical properties are often required for the development of post harvest equipments. The physical properties namely, dimensions, 1000 unit mass, fruit part fraction, arithmetic mean diameter, geometric mean diameter,

some developing countries shows it wide differences in their problems and potential solutions.

Stephane (2005) stated that bio fuels have been under industrial development for over 20 years. Still handicapped by high costs, their future once again looks promising because they might be able to reduce oil consumption and green house gas emissions in the transport sector. This is especially true in Europe, where recently approved directives contain ambitious production volume targets encouraging member states to develop biofuels.

Gobbakka *et al.* (2011) transesterified the non-edible oils of mahua and *jatropha* were using methanol and 1 wt % KOH as the catalyst. The effect of co-solvent and the kinetic study of the transesterification of mahua oil is being reported here for the first time. Kinetics, modeled as a single-step reaction, revealed that the order of the reaction is 2 with respect to the triglyceride concentration and 1 with respect to the methanol concentration in both oils. In the presence of co-solvent, tetrahydrofuran (THF), methanolysis of mahua oil resulted in the increase of the rate constants from 0.08 to 1.17 L<sup>2</sup> mol<sup>-2</sup> min<sup>-1</sup> at 28°C and from 0.43 to 3.18 L<sup>2</sup> mol<sup>-2</sup> min<sup>-1</sup> at 45°C. The corresponding values for *jatropha* oil were found to be 0.50 and 2.76 L<sup>2</sup> mol<sup>-2</sup> min<sup>-1</sup> at 28°C and 1.26 and 4.56 L<sup>2</sup> mol<sup>-2</sup> min<sup>-1</sup> at 45°C.

## 2.2 BIODIESEL FROM *Simarouba glauca*

Devan and Mahalakshmi (2009a) carried out engine tests with the aim of obtaining the performance, emission and combustion characteristics of a diesel engine running on methyl ester of paradise oil (MEPS) and its diesel blends. From the emission analysis it was found that there was a significant reduction in smoke and hydrocarbon emissions by 33% and 22% respectively for MEPS 50 blend and 40% and 27% reductions for MEPS 100. However, there was an increase of 5% and 8% NOx emission for MEPS 50 and MEPS 100 respectively. Brake thermal efficiencies of MEPS and its diesel blends are slightly lower than that of std. diesel. From the engine analysis, it was found that the performance of MEPS and its diesel blends were similar to that of std. diesel.

Devan and Mahalakshmi (2009b) studied the complete replacement of diesel fuel with bio-fuels. For this purpose; bio-fuels, namely, methyl ester of paradise oil and eucalyptus oil were chosen and used as fuel in the form of blends. Various proportions of paradise oil and

surface area, sphericity, aspect ratio, bulk density, true density and porosity has been evaluated. In the study it is found that *Simarouba* kernel has highest oil content (61.04%) as compare to *Jatropha* (45.03%) and *Karanja* (34.67%) kernel. The oil content of *Jatropha* seed is 38.32% whereas the oil content of *Jatropha* fruit, *Karanja* fruit and *simarouba* fruit are 20.12%, 18.45% and 15.28% respectively. The average moisture content of *Jatropha* seed is 7.21% and its average length, width, thickness and 1000 seed mass are 18.83, 1.47, 9.01 mm and 761.50 g, respectively. The size of *Karanja* fruit and kernel are highest as compared to *Jatropha* and *Simarouba* fruit and kernel. Out of these three tree borne oil seeds *Jatropha* fruit is found to be an equivalent sphere.

Anonymous (2011) investigated *simarouba* oil, which can be produced from *simarouba* seeds, for its suitability on a diesel engine. The world is facing crisis due to the dwindling sources of fossil fuels. With ever increase demand for fossil fuel and reserves of fossils fuels next 50 years "Energy Crisis" has cast its dark shadows on the modern humans never before. There is a necessity to find alternate fuels for different industrial needs, automobiles and aircrafts. Different researchers have conducted experiments on vegetable oils as alternative fuels for I.C engines. A single cylindered, verca I diesel engine was selected for this purpose. Different performance curves, TFC Vs BP, BTh Vs BP, with varying loads as well as for different blends are represented. *Simarouba* oil can be alternative for diesel run engines within the range of experiment. The performance is expected to be as good as diesel. Their high viscosity and poor volatility affects the combustion and emissions considerably in diesel engines. Viscosity and volatility of the vegetable oil can be improved by adding ethyl acetate and supercharging the inlet air. It is observed that, apparently, the engine ran smoothly with the *Simarouba* oil. Some more rigorous tests are required to establish the suitability of the *Simarouba* oil in diesel engines.

Dash *et al.* (2008) investigated the physical properties of *Simarouba glauca* L. Fruit and kernel, namely, dimensions, 1000 unit mass, fruit part fraction, arithmetic mean diameter, geometric mean diameter, surface area, sphericity, aspect ratio, bulk density, true density, porosity and angle of repose. The kernel had 8.51% moisture and 61.04% oil content, which is higher than the fruit and shell. The average fruit length, width, thickness and 1000 unit mass were 21.26, 13.81, 11.03 mm; and 1120.16 g, while the corresponding value for kernel were 13.78, 7.77, 6.71 mm; and 330.26 g, respectively. The sphericity and surface area of fruit were 5.8 and 63.36% more, respectively, than those of kernel. Bulk densities of fruits

and kernels were 622.27 and 727.73 kg m<sup>-3</sup>, the corresponding true densities were 931.96 and 1019.3 kg m<sup>-3</sup>, and the corresponding porosities were 33.23 and 28.61%, respectively. The angle of repose of fruit and kernel were 31.35 and 35.02, respectively.

Anil *et al.* (2011) observed that the refining of Simarouba oil result in the improvement of oil quality and making the oil suitable for human consumption, storage and bio-fuel production. Refining of oil (including a series of processes like degumming, alkali refining and bleaching) are aimed to remove the impurities like free fatty acids, phosphatides, metal ions, waxes, oxidation products, colour bodies etc. so as to make oil suitable for edible and storage purposes. The above processes were applied on the *Simarouba glauca* and rapeseed oil to observe the effect of refining on different physico-chemical properties like free fatty acids, iodine value, peroxide value, saponification value, unsaponifiable matter and fatty acid composition.

In the study of Rafiyat *et al.* (2008), *Simarouba glauca* explants were transformed with *Agrobacterium tumefaciens*, carrying beta-glucuronidase (GUS) or green fluorescent protein (GFP) genes. *Simarouba glauca* is a relatively fast growing multipurpose tree, with many medicinal purposes. Simarouba is a medium-sized tree that grows up to 20 meters high and is well suited for warm, humid, tropical regions. Its seeds contain about 60-70% oil that can be converted to biodiesel. The explants were then cultured on co-cultivation medium (MS w/ vitamins+2 mg/L Thidiazuron (TDZ) + 2 mg/L IBA + 4% sucrose + 0.8% Agar at pH 5.7) for three days at 26-28°C and on callus induction medium containing MS+ B5 vitamins with benzyladenine purine (BAP) and Indole-3-butyric acid (IBA). They tested different parameters influencing transformation efficiency using marker genes (GUS and eGFP). The key parameters included the comparison of particle bombardment versus *Agrobacterium*-mediated transformation, wounding explants (to remove the wax on leaves), use of high sucrose + maltose (plasmolysis) and vacuum. About 10 explants were used per plate for the transformation experiments. Preliminary results indicated that *Agrobacterium*-mediated transformation was more efficient than particle bombardment. When placed in vacuum, there is GFP expression on scraped explants and not scraped explants and when placed on plasmolysis, there is GFP expression on the scraped and not scraped leaf explants. Likewise, high frequency of GUS/GFP expression was observed when the leaves were scraped on the adaxial surface.

## CHAPTER 3 MATERIALS AND METHODS

### 3.1 MATERIALS

*Simarouba glauca* seeds were procured from Ramesh forestry, Secunderabad, Andhra Pradesh. Petroleum ether, procured from Rankem Company, India was used as solvent for oil extraction in Soxhlet unit. Food mixer available in the laboratory was utilized for the grinding of seeds. Magnetic stirrer (Make: REMI, Model: 1 MLH), Vortex Mixer (Make: REMI, Model CM 101) were used for the stirring the mixtures. A trial version of Design Expert 8.0.7 was used for optimization by RSM.

### 3.2 METHODS

#### 3.2.1 Collection of Seeds

The simarouba fruits were decorticated with the help of a hammer to obtain kernels. The fruit breaks into two halves. The shells and kernels were separated manually. Then the kernels were collected for further analysis.

#### 3.2.2 Oil Extraction

Kernels of *Simarouba glauca* seeds were dried and grind to fine powder by using domestic food mixer. 100 g of this powder was dissolved in 300 mL of petroleum ether to extract oil in Soxhlet unit by heating it to about 60°C for 6 h. Then the solution was allowed to cool gradually. After that oil was separated for further analysis.

#### 3.2.3 Estimation of Free fatty acids

1 g of oil was dissolved in the neutral solvent which contains 25 ml of diethyl ether, 25 ml of 95% ethanol and 1ml of 1% phenolphthalein. After adding a few drops of phenolphthalein, it was titrated against N/10 KOH. Then it was shaken constantly until the pink colour persists for fifteen seconds.

Govindaraju *et al.* (2009) studied the protein rich (47.7 g/100 g) Simarouba meal in food/feed for its chemical composition with emphasis on protein characteristics and toxic constituents. Simarouba meal contained high calcium (143 mg/100 g) and sodium (79 mg/100 g). Saponins with triterpenoid aglycone (3.7 g/100 g), alkaloids (1.01 g/100 g), phenolics (0.95 g/100 g) and phytic acid (0.73 g/100 g) were the major toxic constituents identified in Simarouba meal. TLC and HPLC results indicated that among different fractions of Simarouba saponins, one dominant fraction accounted for about 28%. Proteins of Simarouba recorded high in vitro digestibility (88%). SDS-PAGE revealed four major protein bands in molecular weight ranges of 20–24, 36–45 and 55–66 kDa. Apart from, glutamic acid (23.43 g/100 g protein) and arginine (10.75 g/100 g protein), simarouba protein contained high essential amino acids like leucine (7.76 g/100 g protein), lysine (5.62 g/100 g protein) and valine (6.12 g/100 g protein). Among nutritional indices, Simarouba meal recorded a good EAA Index (75.02), C-PER (1.90) and PDCAAS (1.0- Adult group).

Prakash *et al.* (2010) demonstrated a suitable process comprising acid pretreatment followed by main base transesterification reaction to produce biodiesel from mixture of Mahua (M) and Simarouba (S) oils with high free fatty acids (FFA). The acid pretreatment reduced the high FFAs of the mixture of oils to around 1% which were then transesterified with methanol and KOH as catalyst at a reaction temperature of 60°C. A genetic algorithm coupled with artificial neural network (ANN-GA) model to obtain the best pretreatment process parameters for bringing down the FFA level of individual vegetable oils to around 1% was modified to include the wide range of oils and validated for mixtures of M and S oils. The quality of biodiesel produced was analyzed by gas chromatography (GC), which indicated above 90% ester conversion. The fuel properties of biodiesel were found to be comparable to diesel and were conforming to the latest biodiesel standards.

There are no scientific reports available for optimization of transesterification of reaction to produce biodiesel from simarouba oil by RSM and also in the mixture of simarouba oil and palm oil. The parameters like alcohol: oil ratio, reaction time and reaction temperature were used as input variable in Box – Behnken design and the values were optimized.

### 3.2.4 Transesterification

The transesterification reaction was carried out with 0.25 v/v methanol-to oil ratio (i.e., 6:1 molar) using 0.7% w/v KOH as an alkaline catalyst. The amount of KOH (7g per litre of pretreated simarouba oil) was arrived at based on the amount needed to neutralize the unreacted acids (i.e., 2mg KOH/g) in the second stage product plus 0.5% for catalyst. The reaction was carried out at 60°C for half an hour. The reaction product was allowed to settle overnight before removing the glycerol layer from the bottom in a separating funnel to get the ester layer on the top, separated as biodiesel (Shashikant and Hifjur, 2006)

CHAPTER 4  
RESULTS AND DISCUSSION

4.1 DETERMINATION OF OIL YIELD

Weight of seed sample = 4000 g  
 Volume of oil extracted = 655 mL  
 Weight of 1 mL of oil = 0.96 g  
 Weight of kernel obtained = 1020 g  
 Weight of oil = Volume of oil x Density of oil  
 = 655 x 0.96 g/ml  
 = 628.8 g  
 Oil in ground sample % =  $\frac{\text{Weight of oil (g)} \times 100}{\text{Weight of sample (g)}}$   
 =  $\frac{628.8 \times 100}{1020}$   
 = 64.21%

4.2 DETERMINATION OF FREE FATTY ACID (FFA) VALUE

Acid value (mg KOH/g oil) =  $\frac{\text{Titre value} \times \text{Normality of KOH} \times 56.1}{\text{Weight of the sample}}$   
 =  $\frac{0.6 \times 0.1 \times 56.1}{1}$   
 = 3.366 g KOH/g oil

4.3 PROCESS OPTIMIZATION OF BIODIESEL PRODUCTION FROM SIMAROUBA OIL:

Table 4.1 Independent variables and levels used for Box – Behnken design

Variables	Symbols	Levels		
		-1	0	1
Oil : Alcohol ratio	M	3	6	9
Feed Temperature (°C)	T	55	65	75
Reaction time (h)	t	8	16	24

Table 4.2 Box – Behnken Design Table for biodiesel production from Simarouba oil

Std	Run	M:OAR	T:TEMP	t:TIME	FFA
14	1	6	65	16	4.99
16	2	6	65	16	4.99
12	3	6	75	24	1.87
11	4	6	55	24	6.99
15	5	6	65	16	4.99
1	6	3	55	16	3.61
6	7	9	65	8	4.74
8	8	9	65	24	5.23
13	9	6	65	16	4.99
2	10	9	55	16	3.36
17	11	6	65	16	4.99
10	12	6	75	8	4.61
9	13	6	55	8	3.12
5	14	3	65	8	3.49
3	15	3	75	16	0.32
7	16	3	65	24	5.23
4	17	9	75	16	3.82

Table 4.3. Regression coefficient of predicted quadratic polynomial model

Source	Sum of Squares	Mean Square	F value	p-value (Prob > F)	
Model	36.10	4.011	38.40	< 0.0001	Significant
M-OAR	2.531	2.531	24.23	0.0017	
T-Temp	5.216	5.216	49.93	0.0002	
t-Time	1.411	1.411	13.50	0.0079	
MT	3.515	3.515	33.65	0.0007	
Mt	0.390	0.390	3.739	0.0944	
Tt	10.92	10.92	104.5	< 0.0001	
M <sup>2</sup>	2.997	2.997	28.69	0.0011	
T <sup>2</sup>	7.888	7.888	75.51	< 0.0001	
t <sup>2</sup>	1.166	1.166	11.16	0.0124	
Residual	0.731	0.104			
Lack of Fit	0.731	0.243			
Pure Error	0	0			
Cor Total	36.83				

Table 4.4. Validation of the model for biodiesel production from *Simarouba glauca*

Oil Alcohol ratio	Temperature	Time (Hr)	FFA	
			Experimental	Predicted
3	75	23	0.07	0.083

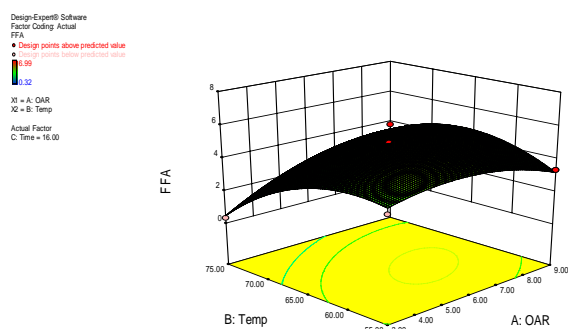


Figure 4.1. Surface plot of free fatty acid value predicted from the quadratic model at a reaction time of 16 h

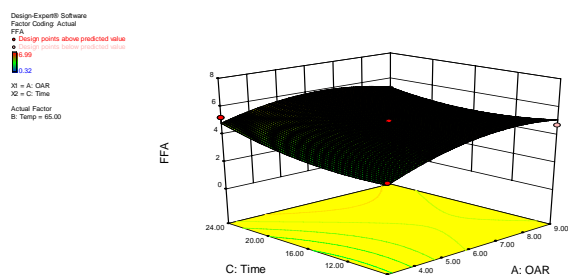


Figure 4.2. Surface plot of free fatty acid value predicted from the quadratic model at a feed temperature of 65°C

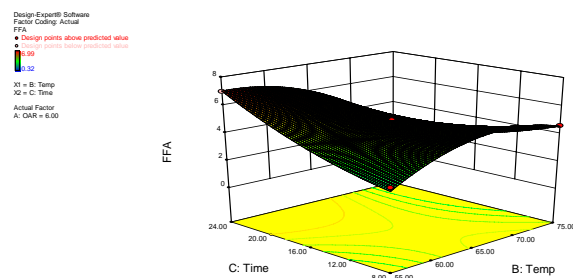


Figure 4.3. Surface plot of free fatty acid value predicted from the quadratic model at an alcohol to oil ratio of 6

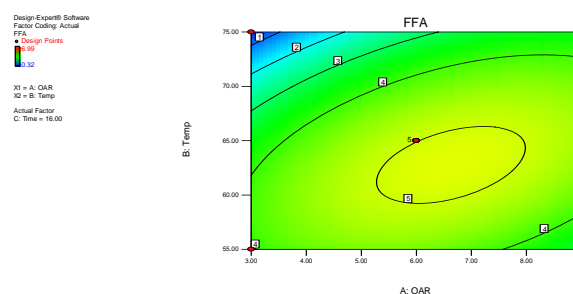


Figure 4.4. Contour plot of free fatty acid value predicted from the quadratic model at a reaction time of 16 h

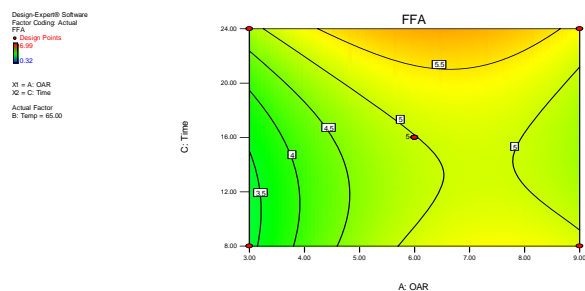


Figure 4.5 Contour plot of free fatty acid value predicted from the quadratic model at a feed temperature 65°C

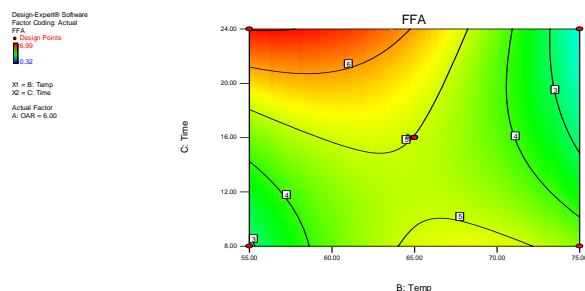


Figure 4.6 Contour plot of free fatty acid value predicted from the quadratic model at an alcohol to oil ratio 6

where  $Y$  is the response (free fatty acid value, mg KOH/g oil);  $x_1$  and  $x_2$  are the uncoded independent variables and  $\beta_0$ ,  $\beta_1$ ,  $\beta_{11}$  and  $\beta_{12}$  are intercept, linear, quadratic and interaction constant coefficients respectively. Design expert trial version 8.0.7 was used for regression analysis of variance (ANOVA). Response surfaces and contour plots were developed using the fitted quadratic polynomial equation obtained from regression analysis, holding one of the independent variables at a constant value corresponding to the stationary point and changing the other two variables. Confirmatory experiments were carried out to validate the equation, using combinations of independent variables which were not part of the original experimental design but within the experimental region. (Table 4.3)

Experimental values obtained for free fatty acid value responses at the design points are given in Table 4.2. Multiple regression coefficients are indicated in Table 4.3 were obtained by employing a least square technique to predict quadratic polynomial model for the free fatty acid value. Analysis of these parameters with the t-test indicated that except  $T^2$ , other linear terms and all quadratic terms had significant effect on the reduction of acid value. However, the interaction terms were found to be non significant. The model was tested for adequacy by analysis of variance. The regression model for data was found to be highly significant with a coefficient of determination as 0.982. Using the coefficients determined, the predicted model for acid value is:

$$\text{FFA} = -61.37 - 0.51 * M + 1.84 * T + 1.21 * t + 0.0312 * M * T - 0.013 * M * t - 0.02 * T * t - 0.09 M^2 - 0.0136 T^2 + 8.22 \times 10^{-3} * t^2 \quad (4.2)$$

From Table 4.3 and Equation 4.2, it could be concluded that the linear and quadratic effects of  $M$  and  $t$  were the primary determining factors of the responses followed by quadratic effect. The relationship between independent and dependent variables of the developed model is shown in Figures 4.1 to 4.6 in the form of contour and surface plots. All Eigen values obtained for the analysis were positive indicating that the stationary point for the response at minimum. The critical values of three variables were found to be 3 methanol-to-oil ratio, 75°C feed temperature and 23 h reaction time locating the stationary point in the experimental region. Verification experiments showed reasonably close value of  $0.0765 \pm 0.0092$  mg KOH/g to the predicted value for the stationary point (0.083 mg KOH/g) and thus confirmed the adequacy of the predicted model (Table 4.4).

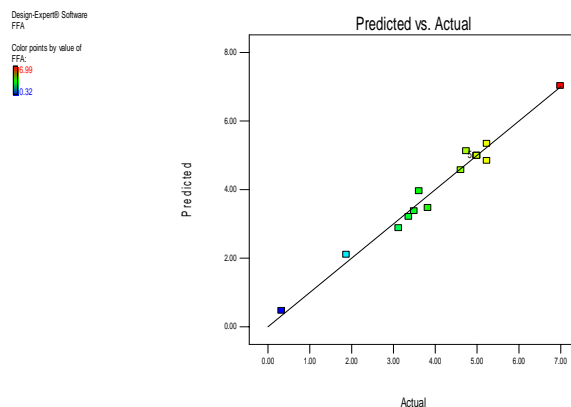


Figure 4.7 Predicted and actual value of biodiesel production from *Simarouba glauca*

A three-level-three-factor Box-Behnken was employed in this study, requiring 17 experiments (Cochran and Cox, 1992). Methanol-to-oil ratio ( $M$ ), reaction temperature ( $T$ ) and reaction time ( $t$ ) were the independent variables selected to optimize the reduction of free fatty acid value (FFA) of crude simarouba oil after pretreatment (Table 4.2). The coded and uncoded levels of the independent variables are given in Table 4.1. Two replications were carried out for all design points except the center point (0, 0, 0) and the experiments were carried out in randomized order.

The experimental data obtained by following the above procedure were analyzed by the response surface regression procedure using the following second-order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{1i} x_i^2 + \sum_{i < j=1}^3 \beta_{1j} x_i x_j \quad (4.1)$$

The responses corresponding to the second-order model indicated that, for low feed temperature, FFA conversion increases with increasing methanol to oil ratio and reaction time (Figures 4.2 and 4.5). Maximum conversions were, therefore, obtained for small methanol amounts, due to the fact that it was the most significant factor with positive effect. However, at higher feed temperature, there seemed to be more effect of increasing methanol amount or reaction time. This could be due to the negative coefficients of catalyst-time and methanol-time interactions (Shashikant and Hijur, 2006).

At low feed temperature, there was a moderate increase in conversion with reaction time, since the time effect was negative and greater than that of feed temperature. For higher feed temperature the increase of conversion with time became smaller (as a result of the positive interaction). Therefore, the operating conditions of large feed temperature and reaction time should be avoided. It was also observed that increasing reaction time beyond 24 hours does not have much effect on reducing the acid value as desired (Figures 4.1 and 4.4). This might be due to the effect of water produced during the esterification of free fatty acids, which prevented further reaction.

As more and more FFAs were esterified by methanol, the reaction might have produced more water with increasing time. It was observed that high amount of methanol (methanol-to-oil ratio of 3) was required during the pretreatment step to bring down the FFA content below 1%. However, in a commercial application, this could be reduced by recovering part of it by fractional distillation of the water-mix, which would be separated from the top after pretreatment. Also it could be possible to further reduce the methanol consumption by continuously removing the water from the mixture during the reaction.

Table 4.5. Fuel properties of simarouba oil

Property	Unit	Simarouba oil	Simarouba biodiesel	Jatropha biodiesel	Karanja biodiesel	Diesel
Density	Kg/m <sup>3</sup>	960	870	880	876	850
Dynamic viscosity	g/m.s	12.9	8.09	4.2592	8.4096	2.21
Kinematic viscosity	mm <sup>2</sup> /s	13.44	9.31	4.84	9.60	2.60
Flash point	°C	142	137	192	187	68
Fire point	°C	147	148	187	177	67
Acid value	mg KOH/g	3.366	0.070	0.24	36.12	0.35

A test case of alkaline-catalyzed transesterification was run using a pretreated sample that had an acid value of 3.366 mg KOH/g. A 3:1 molar ratio of methanol and an alkaline catalyst (0.7% w/v KOH) were used for the reaction. Following this process, a yield of 62% biodiesel was obtained from simarouba oil. The fuel properties of simarouba biodiesel obtained following the above-mentioned procedure are summarized in Table 4.5 along with crude mahua oil, Karanja and Jatropha biodiesel and diesel. It can be seen that the fuel properties of simarouba biodiesel are similar to those of Karanja and Jatropha biodiesel except the dynamic viscosity and the kinematic viscosity. Moreover, simarouba biodiesel had comparable fuel properties with those of diesel and conforming to the latest Indian standards for biodiesel (Becker and Francis (2002), Raheman and Phadatar (2004)).

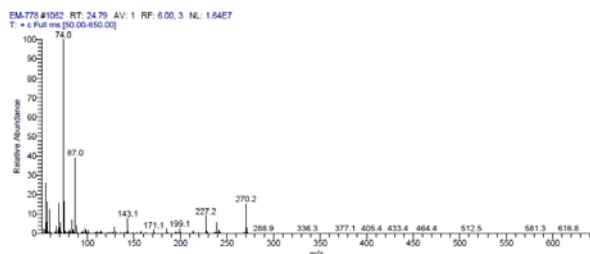


Figure 4.8. Chromatogram for biodiesel obtained from simarouba oil

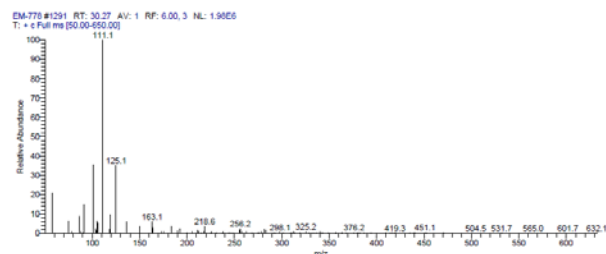


Figure 4.9. Chromatogram for solvent present in simarouba oil sample

The chromatograms for FAME obtained from crude simarouba oil are shown in Figures 4.8 and 4.9. From these spectra, it was found that the amount of oleic methyl ester was 55.74% in biodiesel followed by methyl stearate and palmitate. The  $m/z$  for methyl palmitate, methyl oleate, methyl stearate and methyl linoleate was observed to be 74, 87, 143.1 and 171.1, respectively. The high peak shown in Figure 4.9 at  $m/z$  of 111.1 is n-hexane and should not be confused with other methyl ester peaks. The overall conversion of oil to methyl esters was calculated on the basis of their relative area percentage and was found to be above 62%.

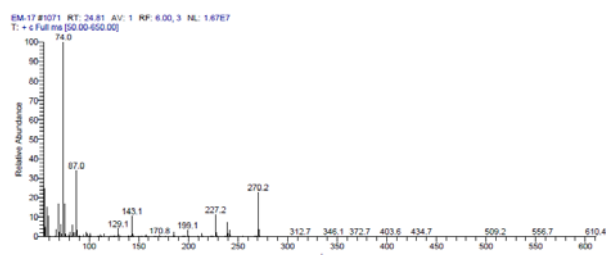


Figure 4.10. Chromatogram for different biodiesel obtained from mixtures of simarouba oil and palm oil

The chromatograms for FAME obtained from mixture of palm and simarouba oils are shown in Figures 4.10. From this spectra, it was found that the amount of oleic methyl ester was 25.44% in biodiesel followed by methyl stearate and palmitate.

## CHAPTER 5 CONCLUSION

In the present study, simarouba oil was extracted by soxhlet method and its free fatty acid value was calculated and identified. The low FFA (3.4%) level of crude simarouba oil makes it potential oil source for the production of biodiesel. The crude simarouba oil was used for the alkali-catalyzed (0.7% w/v KOH) transesterification reaction with methanol. After transesterification step, settling time of minimum one hour was required for removal of methanol-water mixture. A second order model was obtained to predict free fatty acid value as a function of methanol-to-oil ratio, feed temperature and reaction time. The model was found to describe adequately the experimental range studied. This process gave a yield of 62% SOME having properties satisfying Indian standards for biodiesel. The yield of SOME is improved by using a mixture of palm and simarouba oils as lipidic feedstock for FAME production. This process gave a yield of 94% FAME having properties satisfying Indian standards for biodiesel.

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