

CHAPTER 3

VALUE CHAIN OF JATROPHA

3.1. Introduction

This chapter outlines the various stages in the value chain of *Jatropha curcas* for biofuel production. It also provides a comprehensive understanding of each and every stage along with all possible methodologies and technologies developed till date for the production of green diesel. Once the value chain is in place, this chapter would build up the base for the further life cycle study for the calculation of net energy balance and net energy ratio for *Jatropha* green diesel production system. Each and every stage of the value the chain has influence on the LCA result.

3.2. *Jatropha Curcas*

J. curcas is a drought-resistant [88, 89], perennial [90] shrub or small tree [90, 88, 91]. It is a native of Central and South America [88, 90] but has spread beyond its origin [25]. It is cultivated in many tropical [88, 92, 93] and sub-tropical regions of the world [25], which include South-east Asia [88], India and Africa [90, 88].

J. curcas has many uses [90, 94, 47]. Its first commercial application for soap production and for lamps was reported from Lisbon. The seed cake was used as fertilizer for potatoes [88].

It can be used to control erosion, for land reclamation, and as a live fence to keep away farm animals as its leaves and stems are toxic to animals [94, 47, 90, 92]. The other uses of this plant include manufacture of soap, cosmetics [90, 47], lubricants, candles, and as a source of purgative, astringents and coloring dye [95]. However, today *Jatropha curcas* is

mainly cultivated for the production of oil as a fuel substitute [88, 89, 95, 89]. The Portuguese were the first to introduce *Jatropha curcas* in Asia and Africa as an oil-yielding plant [95, 88]. *Jatropha* contains oil in the form of triacylglycerols (TAG) [96], which serve as a promising biodiesel feedstock [96, 90, 89], while the press cake or the seed cake can be digested to produce biogas (CH₄), or can even be used as an organic fertilizer [94] or may be used as animal feed after detoxification [97, 47].

Apart from being an important fuel substitute, *Jatropha* biodiesel also helps to counter greenhouse gas accumulation. Like all trees, it fixes atmospheric carbon, stores it in wood and assists in the buildup of soil carbon [47]. Therefore, it has been promoted extensively as an energy crop for biodiesel production across the world [98].

3.2.1. Taxonomy, Nomenclature and Plant Description

3.2.1.1. Taxonomy & Nomenclature

Jatropha curcas is one of approximately 175 species. According to some authors, it is one of 175-200 species [99] in its genus [90, 25]. It is a member tribe Joannesieae [91, 25] of Crotonoideae [25] of Euphorbiaceae family [90, 88, 96, 94, 47, 40, 91, 25, 100, 92].

The genus name *Jatropha* is derived from the Greek word *jatr'os* (doctor) and *troph'e* (food) [91, 93, 25, 100], which implies medicinal uses [91, 93, 25]. In English, it is known as “physic nut” or “purging nut”, in Dutch as “Purgeer-noot” or “Schijt-noot” and in Arabic as “habelmeluk” [93]. Current name is *J. curcas* Linnaeus, which was given by Linnaeus [25]. Dehgan and Webster postulated the physic nut (*J. curcas* L.) to be the most primitive form of the *Jatropha* genus. Species in other sections evolved from the physic nut or another ancestral form, with changes in growth habit and flower structures [25].

According to Dehgan and Webster and Schultze-Motel, the other synonyms of the physic nut are: *Curcas purgans* Medik, *Ricinus americanus* Miller, *Castiglioni lobata* Ruiz and Pavon., *Jatropha edulis* Cerv., *J. acerifolia* Salisb, *Ricinus jarak* Thunb., *Curcas adansoni* Endl., *Curcas indica* A. Rich., *Jatropha yucatanensis* Briq., and *Curcas curcas* (L.) Britton & Millsp. [25].

In India, it is represented by nine species viz. *Jatropha curcas* L., *Jatropha heynei* Balak., *Jatropha gossypifolia* L., *Jatropha glandulifera* Roxb., *Jatropha intergerrima* Jacq., *Jatropha nana* Dalz. and Gibs, *Jatropha podagrica* Hook., *Jatropha multifida* L., and *Jatropha tanjorensis* Ellis & Saroja. Out of these nine species, *J. intergerrima* Jacq., *J. podagrica* Hook. and *J. multifida* L. are grown in gardens for ornamental purposes, while *J. curcas* L. and *J. gossypifolia* L. are grown for other varied uses. These species have been naturalized in different agro-climatic conditions in the country since their introduction from the American Continent. Species like *J. glandulifera* Roxb., and *J. nana* Dalz. and Gibs. are however restricted in distribution, being mostly confined to Deccan Peninsular regions [95].

3.2.1.2. Jatropha Plant Description

The physic nut, by definition, is a small tree or large shrub, which can reach a height of three to five meters, but under favorable conditions it can also attain a height of 8 or 10 m [25, 91]. The plant shows articulated growth, with a morphological discontinuity at each increment. The branches contain latex. Figure 3.1 shows a typical *Jatropha curcas* plantation.



Figure3. 1: *Jatropha curcas* Trees [101]

Below is the description of each part of *Jatropha* plant:

- a. **Roots:** Seedlings give rise to five roots, one central and four peripheral roots. Plants grown through vegetative propagation do not form tap roots [91].
- b. **Leaves:** *Jatropha curcas* leaves are five to seven lobed, hypostomatic and stomata are of paracytic (Rubiaceous) type. The trees are deciduous, which shed their leaves in dry season [91].
- c. **Stems:** *Jatropha curcas* has succulent stem with low wood density. This property of *Jatropha* stem along with conservative transpiration rate helps to retain water, and thus, to adapt during drought stress [102].
- d. **Flowers:** Flowers are greenish yellow in color [25], and occur during the wet season. Though summer and autumn are two peak flowering seasons, in permanently humid regions flowering occurs throughout the year. The plant is monoecious, produces male and female flowers in the same inflorescence and flowers are unisexual [25, 91] with very

rare hermaphrodite flowers. In conditions, where continuous growth occurs, an unbalance of pistillate or staminate flower production results in a higher number of female flowers [91] . Both self and cross-pollination occurs in *Jatropha* [25].The rare hermaphrodite flowers can be self pollinating. The flowers are pollinated by insects, especially honey bees. The inflorescence is axillary paniculate polychasial cymes [25]. Each inflorescence yields a bunch of approximately 10 or more ovoid fruits [91].

- e. **Fruits:** The seeds mature in about 3–4 months after flowering. Three, bivalved cocci are formed after the seeds mature and the fleshy exocarp dries. Figure 3.2 shows a *Jatropha* fruit. In good rainfall conditions nursery plants may bear fruits after the first rainy season, and directly sown plants after the second rainy season [91]. The dry fruits, with 2-3 seeds, remain on the branches and the hull or shell becomes hard and black [103, 39]. The maturity stage of the fruits at the moment of collection is reported to influence the fatty acid composition of the oil [104].

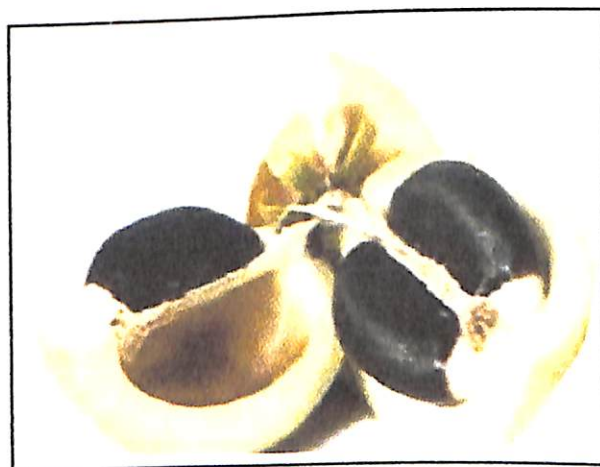


Figure3. 2: *Jatropha* Fruit [101]

- f. **Seeds:** The seeds of physic nut are a good source of oil, which can be used as a diesel substitute. Figure 3.3. shows *Jatropha* seeds. There are

about 1375 seeds/kg on an average and weight per 1000 seeds is about 727 g. However, the seeds of *Jatropha curcas* are, in general, toxic to humans and animals. Curcin and phorbol esters are a few toxic agents. Therefore, before *Jatropha* oil can further be used for industrial applications or in human medicines, complete removal of toxins is necessary [91].



Figure3. 3: Jatropha Seeds [101]

3.3.Comprehensive Value chain of *Jatropha curcas*

The complete value chain of *Jatropha* for biofuel production contains following major stages (Figure 3.4 shows the value chain of *Jatropha* for biofuel production):

1. *Jatropha* Cultivation & Harvesting
2. Oil Extraction
3. Oil & Seed cake processing
4. End combustion of Green diesel

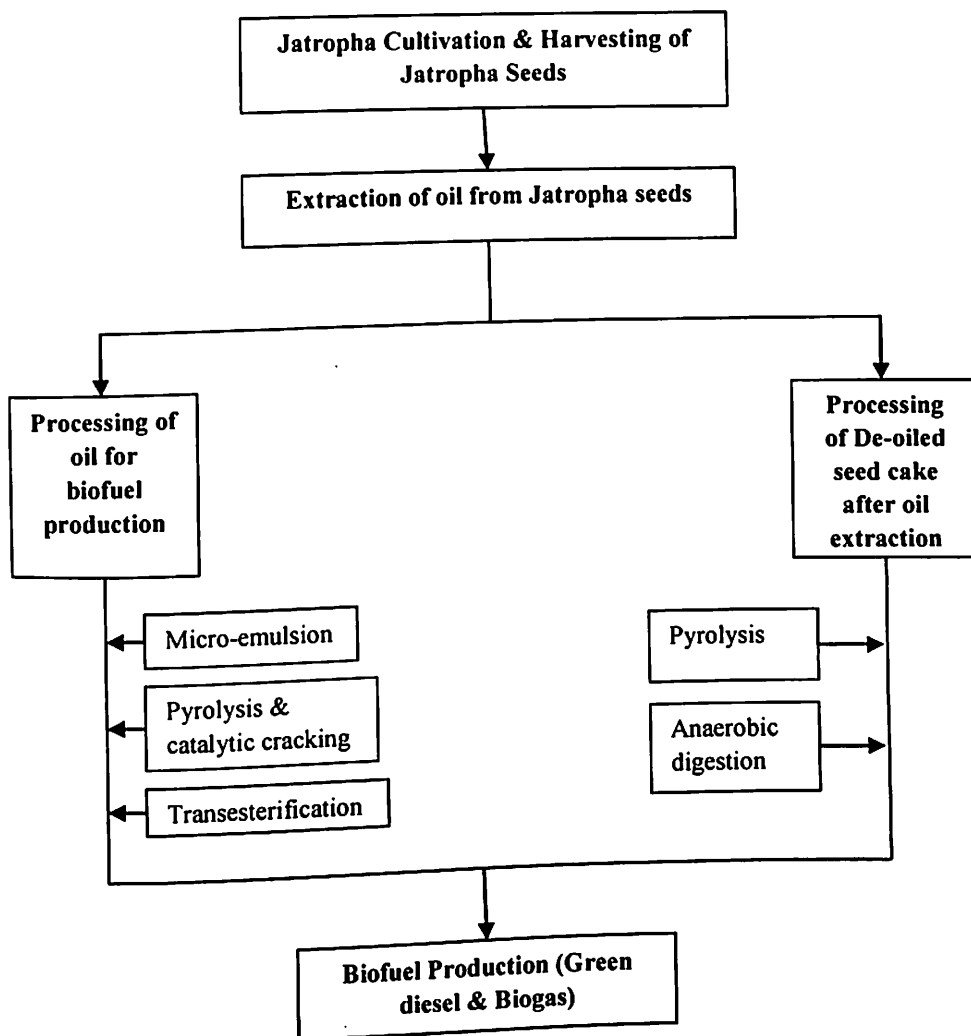


Figure3. 4: Value Chain of Jatropha for Biofuel Production

3.3.1. Jatropha Cultivation & Harvesting

3.3.1.1. Soil and Climatic requirements

Jatropha is a drought resistant, hardy crop, and is easy to establish [94, 47]. It is a highly adaptable species, but its strength as a crop comes from its ability to grow on very poor and dry sites [91]. It can grow in marginal soils with pH up to 9 [94]. It grows on well-drained soils with good aeration. In heavy soils, the root formation is reduced. It is well adapted to arid and semi-arid conditions and grows almost anywhere except

waterlogged lands, even on gravelly, sandy and saline soils. It can even thrive on the poorest stony soil and in the crevices of rocks [91].

J. curcas has high ecological adaptability, thus, allowing to grow in a wide range of conditions [94, 91]. Regarding climate, *Jatropha* is found in the tropics and subtropics, and likes heat, although it does well even in lower temperatures and can withstand a light frost. It can grow under a wide range of rainfall regimes from 250 to over 1200 mm per annum. In low rainfall areas and in prolonged rainless periods, the plant sheds its leaves as a counter to drought, and can stand long periods of drought by reducing transpiration loss [91].

3.3.1.2. Propagation methods

Jatropha grows readily from seeds or cuttings; however, trees propagated by cuttings show a lower longevity and possess a lower drought and disease resistance than those propagated by seeds. This might be due to the absence of true taproots in the trees produced from cuttings, and hence are fewer droughts tolerant. Rather trees from cuttings produce pseudo-taproots that penetrate only 1/2 to 2/3rd the depth of the soil in comparison to the true taproots produced in trees grown from seeds [91, 25]. In better rainfall or good moisture condition the plantation could also be established by direct seeding [91]. Wider spacing between the plants is reported to give larger yields of fruit, at least in early years [91].

3.3.1.3. Harvesting

The fruits are handpicked or harvested by hitting the fruits with a long stick. At times, older trees were harvested by shaking the tree/branches [103, 39].

3.3.2. Oil Extraction

The oil content in Jatropha seed ranges from 25% to 40% by weight and in the kernel itself ranges from 45% to 60% [105]. In the second step of the production chain for bio-diesel, the oil contained in the seeds has to be expelled or extracted. The products obtained after extraction are Jatropha oil and seed or kernel cake [104].

3.3.2.1. Decortication

The collected fruits are sun dried for processing and decorticated to get the seeds [39, 103]. Decortication is the action of separating the shell/seed coat from the seed or kernel, prior to milling and extracting the oil from the kernel. The decorticated oil seed give maximum oil yield in comparison to un-decorticated seeds. The decorticating of Jatropha fruits means breaking and complete removal of the seed coat/shell, and taking out the seed without causing damage for oil expression [103].

Traditionally, decortication or shelling of Jatropha fruits is done by brick, stone or wooden mallets or by direct removal of seeds with one's fingers. The dried fruits are placed in a thin layer on a hard surface i.e. on a table, or on a concrete floor and a small wooden board is moved over them. While pressing it down, the fruit shell splits and the seeds come out. However, this manual process of decortication is time consuming , labor intensive and results in serious injury to human fingers, coupled with low output rates. Moreover, quantity and quality of out-turn depends upon the skill of the operation [103].

Considering all these benefits, Jatropha production and processing must be mechanized and properly improved to aid profits and reduce losses. Keeping the same in mind, a manually operated Jatropha fruit decorticator was designed, constructed and tested. The decorticator does not require electricity for its operation; hence, the problem of the frequent power

outages that characterize in India has no effect on it. Also, because of its cheap cost to manufacture from locally-available materials, it is likely to satisfy a niche market in India and other developing countries [103].

The initial moisture content of dried fruit is around 7.97% dry basis, and corresponding bulk density, true density and porosity were reported as 278 kg/m³, 546 kg/m³, and 49.08% respectively [103]. The increase in moisture content increases the average length, width, thickness, mass and surface area of the fruit [39]. The moisture content of the fruits and concave clearance between concave sieve and rotating blades, significantly affect the performance indicators. The decortication efficiency of the machine decreases with increase in fruit moisture content, while percentage of broken seed with dust decreases with increase in moisture content [103].

3.3.2.2.Oil extraction Methods

Seeds are also dried well before oil extraction. Seed can be dried in the oven at 105 °C or in the sun for 3 weeks [104]. For extraction of the Jatropha oil from the seeds two main methods have been identified: (i) mechanical extraction (ii) chemical extraction [92, 104].

1) Mechanical extraction

For mechanical extraction of the oil from the seed, either a manual ram press or an engine driven screw press can be used. Ram presses extract only 60 to 65%, while engine driven screw presses extract 75 to 80% of the available oil. The oil extraction can be increased by subjecting to a different number of extractions through the expeller. Up to three passes is common practice. Pretreatment of the seeds, like cooking, can increase the oil yield of screw pressing up to 89% after single pass and 91% after dual pass [104] .

2) Chemical extraction

a. n-Hexane solvent extraction method

The n-hexane method is the most common method for oil extraction from *Jatropha*, and it results in the highest oil yield. But this method has certain disadvantages like, it takes a lot of time, and since it is a hazardous and inflammable chemical it impacts human health as well as environment (generation of wastewater, higher specific energy consumption and higher emissions of volatile organic compounds) [104].

However, the new generation n-hexane extraction units are very efficient and produce far less environmental burdens than the older units. In place of n-hexane, bio-renewable solvents, as bio-ethanol and isopropyl alcohol, can be used to overcome the problems by n-hexane, but further research on these alternative solvents is recommended on their commercial viability [104].

b. Aqueous oil extraction and aqueous enzymatic oil extraction

Aqueous enzymatic oil extraction is more efficient process than plain aqueous oil extraction. Use of ultrasonication, as a pretreatment before aqueous oil extraction and aqueous enzymatic oil extraction, is found to be useful in the case of extraction of oil from the seeds of *Jatropha curcas* L. It also reduces the process time.

The maximum yield of 74% was obtained by ultrasonication for 5 min, followed by aqueous enzymatic oil extraction, using an alkaline protease (commercially available) at pH 9.0. While the use of ultrasonication for 10 min at pH 9.0, followed by aqueous oil extraction, gave a yield of only 67% [106]. Aqueous enzymatic oil extraction greatly reduces the problems faced by n-hexane [104].

c. Enzyme assisted three phase partitioning (TPP)

The novel approach of combining a recently developed technique of TPP with enzyme pretreatment (protease enzyme with main component being protease enzyme) and sonication constitute an efficient procedure for obtaining oil from *Jatropha* seed kernels [107]. In this solvent extraction process, called three phase partitioning (TPP), appropriate amounts of ammonium sulphate and t-butanol were added to *Jatropha* slurry. This led to the formation of three distinct phases: upper organic phase, lower aqueous phase and interfacial precipitate (consisting mostly of proteins). The oil was found in the organic solvent phase and could be recovered by evaporating the t-butanol.

TPP is simple to carry out, has short processing time (about 2 hours), and is easy to scale up [107]. Enzyme pretreatment (as it is well established that oil bodies in plants are trapped in the meshwork of proteins and cellulose/ hemicellulose structures) and sonication (smaller particle size was found to give higher yields and sonication is an efficient way for breaking up bigger particles into smaller ones) increased the yield up to 97% [107].

t-Butanol has a higher boiling point (84°C) than hexane (69°C), hence, addition of volatile organic solvents to the atmosphere during TPP will be much lower, even if open systems are used. Moreover, unlike the soxhlet extraction, which is carried out for 24 hours, the TPP method takes only about 2 hours [107].

3.3.2.3. *Jatropha* oil

Depending on the variety, the decorticated seeds contain 40–60% of oil, which is used for many purposes, such as, lighting, as a lubricant, for making soap and most importantly as biodiesel [91]. *Jatropha* oil contains approximately 24.60% of crude protein, 47.25% of crude fat, and 5.54%

of moisture contents [91]. The composition and characteristics of the crude *Jatropha* oil are given in Table 3.1.

Table3. 1: Fatty Acid Composition and Important Properties of Straight *Jatropha curcas* Oil [108].

S No.	Properties of the <i>Jatropha curcas</i> oil	
1	Fatty acid composition (%)	
	Saturated	
	Palmitic acid C16:0	16.0
	Stearic acid C18:0	6.5
	Unsaturated	
	Oleic acid C18:1	43.5
	Linoleic acid C18:2	34.4
2	Specific gravity	0.920
3	Viscosity (cSt) at 40 °C	18.2
4	Flash point (°C)	174
5	Calorific value (MJ/kg)	38.5
6	Acid value (mg KOH/gm)	3.8
7	Free fatty acid (%)	1.9

The other fatty acids include capric acid, myristic acid (C14:0), palmitoleic acid (C16:1), linolenic acid (C18:3), arachidic acid (C20:0), behenic acid (C22:0), cis-11-eicosenoic acid (C20:1) and cis-11,14-eicosadienoic acid (C20:2) [109].

Jatropha curcas oil contains more than 75% unsaturated fatty acid [109, 104], which is reflected in the pour and cloud point of the oil. The fatty

acid composition of *Jatropha curcas* oil is dominated by oleic acid (C18:1) and linoleic acid (C18:2) [104]. The oil, with high percentage of monounsaturated oleic and polyunsaturated linoleic acid, has a semi-drying property (partially hardens when the oil is exposed to air). This semi-drying oil could be an efficient substitute for diesel fuel [91]. The JCL oil meets the quality standard of rapeseed as a fuel [104].

3.3.3. Oil & Seed Processing

3.3.3.1. Oil Processing

The direct use of neat oil or its blend with conventional diesel fuel in a suitable ratio is possible, but leads to technical problems because of their high viscosity, polyunsaturated nature [38, 15, 110], high density and flash point in comparison to petroleum diesel [111]. This results in slow or poor fuel atomization [15, 111]; starting problem, engine choking [111], low stability against oxidation due to polyunsaturated, and low volatility which leads to incomplete combustion and thus high amount of ash formation takes place [110, 15].

Two strategies have been used to overcome these problems [88, 112], i.e., either adaption of the engine to the fuel or adaption of the fuel to the engine. As the second strategy seems to be more practicable in comparison to the first one, accordingly, neat oil must be processed so as to acquire the properties necessary to be directly used in current diesel engines [110, 15]. The possible processes are pyrolysis (or cracking), micro-emulsification, transesterification and [38, 15, 110], hydrogenation [113].

A. Oil Processing Methods

1) *Micro-emulsion of oils*

Short-chain alcohols like ethanol and methanol are used for micro-emulsions. Studies have been conducted on reducing high viscosities of

vegetable oils by forming micro-emulsions with short-chain immiscible alcohols like methanol and ethanol and ionic or non-ionic amphiphiles [38]. Though micro-emulsion of vegetable oil lowers their viscosity, but has been found to result in irregular sticking of injector needle and heavy carbon deposits due to incomplete combustion of the oil [114].

2) *Pyrolysis and catalytic cracking*

Conversion of one substance to another by heating, sometimes with the aid of catalyst, in the absence of air or oxygen to yield smaller molecules is known as pyrolysis. The liquid fuel produced from pyrolysis contains alkanes, alkenes, alkadienes, cycloalkanes, alkylbenzenes, carboxylic acids, aromatics and small amounts of gaseous products, similar chemical components to conventional petroleum diesel fuel [38]. The pyrolyzed vegetable oil has low viscosity, high cetane number. They have acceptable amounts of sulphur, water and sediment contents and copper corrosion values, but their carbon residues, ash contents and pour points are not in acceptable range [114].

3) *Transesterification*

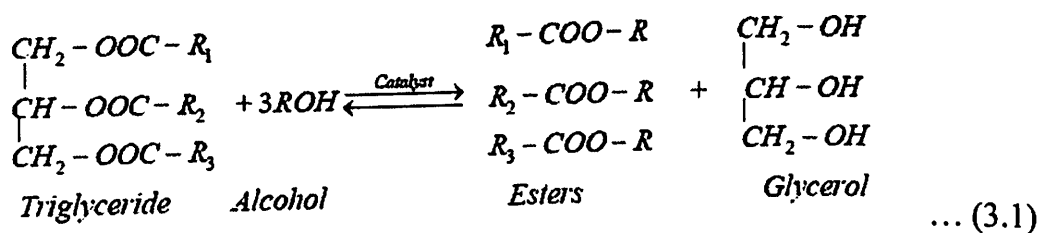
Micro-emulsification, pyrolysis or catalytic cracking, both are cost intensive and produce a low quality biodiesel. Transesterification is the most usual method to convert oil into biodiesel [115], and is the best choice as fatty acid (m) ethyl esters (biodiesel), produced by this process have their physical characteristics very close to those of diesel fuel. Moreover, it is a relatively simple process [38].

In a combustion analysis of *Jatropha* based biodiesel, it was found that various properties of *Jatropha* oil can be improved by the process of transesterification, thus, making it comparable to petroleum diesel. It lowers the flash point, decreases the viscosity, thus making it suitable for use in diesel engine [116].

Transesterification converts raw and viscous lipid (triacylglycerols/free fatty acids) to lower molecular weight fatty acid alkyl esters [117]. The alkoxy group of an ester compound is exchanged by an alcohol (alcoholysis), carboxylic acids (acidolysis) [38] or an ester (interesterification). Only alcoholysis and inter-esterification have gained importance, and are used to produce biodiesel [115]. Thus, it is a reaction between the parent oil (triglyceride) and a short chain alcohol, in the presence of a catalyst. Fatty acid methyl esters (FAME) and glycerol are the products of the reaction [117].

Ethanol can be produced by fermentation process, thus is more renewable, and also less toxic. In spite of this, methanol being cheaper, more reactive and produce more volatile fatty acid methyl esters, is preferred over ethanol [115].

The reaction rate and yield can be improved by use of a suitable catalyst [38]. The catalyst can be acidic, basic or enzymatic in nature [117]. Equation (3.1) shows the transesterification reaction of triacylglycerols with alcohol to produce esters (FAME) and glycerol in the presence all the three types of catalyst.



Few examples of the catalyst used for transesterification are: (1) alkaline-catalyst includes potassium hydroxide, sodium hydroxide and sodium methoxide, (2) acid-catalyst includes hydrochloric acid, sulphuric acid, sulfonic acid [115, 38] and phosphoric acid; (3) enzymatic-catalyst include lipases [115, 38], (4) inorganic heterogeneous catalyst (solid phase

catalyst) [115]. Table 3.2 shows comparison of different catalysis techniques.

a. Base catalysis

The optimum condition of alkali base catalyzed transesterification for *Jatropha curcas* oil requires more catalyst and methanol. The optimum NaOH to oil ratio and the optimum methanol to oil ratio were 3.3% w/w and 70% w/w respectively for *Jatropha* oil. The reason for higher consumption of catalyst NaOH and methanol in the transesterification process of *Jatropha* oil is considered to be free fatty acids (FFA). A high FFA in the oil deactivates the catalyst NaOH, and the addition of excess amount of NaOH as compensation gives rise to the formation of emulsion, which increases viscosity, leads to the formation of gels and the problems of glycerin separation and loss in ester yield [118]. Therefore, coexistence of FFA in the oil is one of the reasons for low yield of base catalyst transesterification of *Jatropha* oil [118].

Because of the dangers inherent in handling metallic potassium, due to its high heat of reaction with methanol, it is preferable to use metal alkoxides (eg. Sodium methoxide) in methanol, in place of metal hydroxides (NaOH, KOH). Alkaline metal alkoxides (CH_3ONa for methanolysis) are the most active catalysts since they give very high yields (>98%) in short reaction times (30 min), even if they are applied at low molar concentrations (0.5 mol %). However, they require the absence of water, which makes them inappropriate for typical industrial processes [119].

Table3. 2: Comparison of different Catalysis Techniques

Parameters	Base catalysis	Acid catalysis	Enzymatic catalysis
Scale of Application	Most widely used process. Currently, practically 100% of biodiesel is produced by the alkaline process.	Acid catalysts are rarely used on the industrial scale because of their corrosive nature.	Enzymatic technology seems to be starting its application in industrial scale. For large scale production this may not be economically viable due to high enzyme production costs [117, 38].
Rate of reaction	It is a faster reaction [117].	The reaction is slow. Speeding up the acid catalysed reaction requires an increase in temperature and pressure making it prohibitively expensive at large scale [117].	Enzyme catalyzed reactions are slower than the alkaline catalyst. There is a risk of enzyme inactivation due to methanol. Benefit includes, moderate reaction conditions, thus less energy intensive [117] and does not even run the reaction to completeness.
Effect of alcohol	Since it is reversible reaction, the rate of forward reaction increases with addition of more alcohol.	Since it is reversible reaction, the rate of forward reaction increases with addition of more alcohol.	If methanol is in a relatively high amount with respect to oil, it may inhibit and deactivate a large proportion of lipase. Thus, lower alcohol to oil ratio requires for production [117].
Effect of free fatty acids (FFA) content	Alkaline reaction is limited by FFA content [117], therefore for alkali transesterification FFA amount should not exceed a certain limit. Alkaline catalysis is preferred over acid catalysis for oil samples containing FFA below 2.0% [114].	It is suitable for transesterification of oils containing high levels of FFA [117]. In any case, acid catalyst is the recommended process when the starting materials have a high concentration of FFA. Since it is more corrosive, its yield is lower in comparison to base catalyst.	It is a viable method for parent oils containing high levels of free fatty acids as they can also be converted to alkyl esters [117].

Parameters	Base catalysis	Acid catalysis	Enzymatic catalysis
Downstream recovery	FFA result in saponification, and also consume a lot of the base catalyst, as a result makes downstream recovery difficult [115, 117]. The process also requires the absence of water, which makes them inappropriate for typical industrial processes [38].	No soaps are formed, if the reagents are moisture free [115, 117].	Easier product recovery. If the lipase is immobilized, it can be easily separated from the reaction mixture by filtration, or when the lipase is in a packed bed photobioreactor (PBR), no separation is necessary after transesterification [117].
Effect on environment	It is not environmental friendly, because it consumes lot of water during washing, in the purification step. Moreover, byproduct glycerol, formed during the reaction, is usually contaminated with alkaline catalysts, thus, before it could be further used, it needs to be purified.	It environmental effects are similar to base catalyst.	The subsequent separation and purification of biodiesel is easier than with alkaline catalysts. Immobilization also increases the stability of the lipases and the potential for repeated use.

b. Acid catalysis

Acid catalysts could be used in conjunction with base catalysts (two stage process). This two stage process allows the use of low-cost feedstock like waste oil with high content of free fatty acids. The acid catalysts are used in the primary stage to convert free fatty acid to methyl esters, followed by a base catalyst process to convert the remaining triglycerides to methyl esters [110].

The FFA and moisture contents have significant effects on the transesterification of glycerides with alcohol using catalyst. The high FFA content (>1%w/w) will happen soap formation and the separation of products will be exceedingly difficult, and as a result, it has low yield of biodiesel product. The acid-catalyzed esterification of the oil is an alternative, but it is much slower than the base-catalyzed transesterification reaction. Therefore, an alternative process such as a two-step process was investigated for feedstock having the high FFA content, in which first step of the process for reducing the FFA content of *Jatropha* oil to below 2% [118].

Therefore, a two step process i.e., acid-catalyzed esterification process, and followed by base-catalyzed transesterification process, was selected for converting *Jatropha* oil to methyl esters of fatty acids. The first step was acid esterification and pretreatment for removing FFA in the oil, which is mainly a pretreatment process, which could reduce the FFA. It was reported that to get complete FFA esterification in some vegetable oils, could be done in the reaction temperature 50 °C. The process was intended to convert FFA to esters using an acid catalyst (H_2SO_4 1% w/w) to reduce the FFA concentration of *Jatropha* oil below 2%. Second step was alkali base catalyzed transesterification [118].

Moreover, in many cases *Jatropha* oil quality deteriorates gradually due to improper handling and inappropriate storage condition. It was known that improper handling of *Jatropha* oil would cause the water content increase. In addition, exposing the oil to open air and sunlight for long time would affect the concentration of FFA increase significantly to high level of FFA above 1%, as in *Jatropha curcas* seed oil extraction, *Jatropha* oil is stored at long time prior to utilization. The FFA amount of *Jatropha* oil varies and depends on the quality of feedstock [118].

Without proper handling and storage, the process causes various chemical reactions, such as, hydrolysis, polymerization, and oxidation. Therefore, the physical and chemical properties of the *Jatropha* oil change during handling and storage [118]. The percentage of FFA has been found to increase due to the hydrolysis of triglycerides in the presence of moisture and oxidations. Degradation of the *Jatropha* oil results in higher concentration of FFA. *Jatropha* oil contains higher concentration of unsaturated fatty acids, which are mainly linoleic acid (18:2) and oleic acid (18:1), where the number before the colon represents the total number of carbons; the number after the colon is the number of double bonds. The oxidation of the unsaturated fatty acids component in the *Jatropha* oil might occur easily and it could lead to degradation of the oil. The reason for auto oxidation is due to the presence of double bounds in the chains of unsaturated fatty acids compounds [118].

Chemical catalyzed transesterification does have its disadvantages in that the process is energy intensive, the catalyst needs to be removed from the product, alkaline water from washing requires remediation, water and free fatty acids result in loss of product due to saponification and recovery of glycerol is difficult [117].

c. Enzymatic transesterification

Enzymatic technology seems to be starting its application in industrial scale. Recently, it has been claimed that this technology has been applied to the industrialization with a capacity of 20,000 tons/year in China, and this is the first industrial scale with lipase as the catalyst in the whole world to date. There are two major categories of enzymatic biocatalyst: (1) extracellular lipases (i.e. the enzyme has previously been recovered from the live-producing microorganism broth and then purified). The major producer microorganisms are *Mucor miehei*, *Rhizopus oryzae*, *Candida Antarctica* and *Pseudomonas cepacia*; (2) intracellular lipase which still remains either inside or in the cell-producing walls; in both cases the enzyme is immobilized and used, which eliminates downstream operations of separation and recycling the lipase [12]. Figure 3.5 shows the flow diagram of enzyme mediated alcoholysis for FAME production.

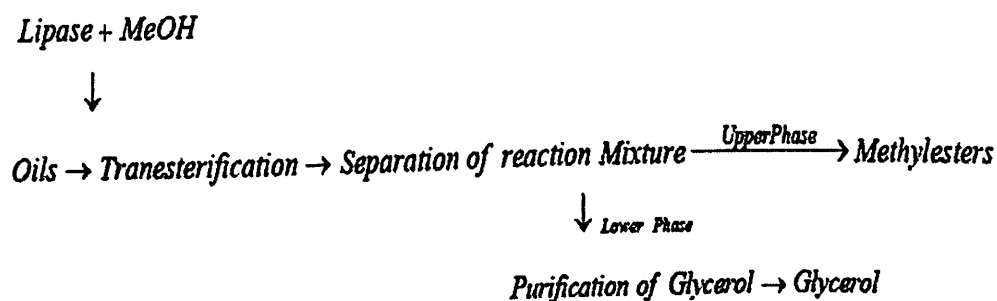


Figure3. 5: Flow Diagram of Enzyme Mediated Alcoholysis for FAME Production
[117]

To reduce the deactivating effect of methanol some authors propose the use of solvents for methanol and oil, for example 1, 4-dioxane. In this regard, t-butanol seems to be the most suitable solvent for an industrial-scale alcoholysis with methanol. Lipases are repeatedly reused without activity losses in reaction systems with t-butanol as organic solvent.

Another alternative consists of a stepwise addition of methanol to the reaction mixture [110].

Glycerol produced during the alcoholysis is insoluble in oil and readily adheres to the immobilized lipase surface thus diminishing enzyme activity. Removal of glycerol can be a complex process and may impede the continuity of larger scale operations [117]. There is also a risk that glycerol inhibits the lipase by covering it, due to its accumulation in the reaction mixture. Some researchers claim that part of the activity loss of the lipase may be due to the presence of glycerol in the reaction mixture. They, therefore, suggest its elimination in situ by dialysis, or by using isopropanol to extract it. However, a better alternative may be to carry out the transesterification in t-butanol. This solvent dissolves the glycerol and increases alcohol solubility as mentioned above [110].

d. Heterogeneous solid catalysts

The conventional industrial production of biodiesel is through transesterification of crude oil with a homogeneous strong base catalyst such as NaOH and KOH. After reaction, recovery of glycerol, removal of base catalyst from products, and treatment of alkaline wastewater are costly and non-environmental. Furthermore, a homogeneous base catalyst is ineffective for production biodiesel from high acid-value crude oils due to the formation of soap.

Tan et al [120] reported a catalyst-free biodiesel production method, using waste palm cooking oil as raw material and supercritical methanol. But the method has a high cost in reactor and operation (due to high pressures and high temperatures), and high methanol consumption (e.g., high methanol and crude-oil molar ratio of 40:1). Therefore, heterogeneous solid catalysts were used for the transesterification process, where a better separation and reuse of the catalysts without saponification were achieved [105].

Preparation and application of solid super base catalysts are an emerging area that is attracting more and more attention, because the catalysts are easily separated for reuse and possess a high activity for various reactions under mild conditions. They can replace homogeneous base catalysts in order to minimize the production of pollutants. LDHs (Layered double hydroxides) are important inorganic materials with layered structure and anion exchanged capacity. As classical solid base materials, calcined LDHs are widely used as catalyst in the production of biodiesel [105].

Solid base nanocatalyst derived from hydrotalcites with Mg/Al molar ratio of 3/1 was synthesized by a co-precipitation method using urea as precipitator and with microwave-hydrothermal treatment (MHT), followed by calcination. Owing to its strong basicity, the catalyst was used for the transesterification of Jatropha oil. Biodiesel yield of 95.2% was obtained and the biodiesel properties were close to those of the German standard (DIN V 51606). The main reasons for catalyst deactivation were the surface absorption of by-product glycerol as well as the collapse of the layered structure. After removing the glycerol on the surface, the catalyst was reused for 8 times [105].

e. Supercritical Method

Transesterification reaction without using any catalyst requires a high temperature above the critical temperature of alcohol, and this is called as supercritical method. By applying extreme pressure and temperature, alcohol (ethanol/methanol) is turned into a supercritical fluid state. The common reaction temperature is more than 250 °C, as the critical temperature of methanol is 240 °C. In this extreme environment, liquid methanol reaches critical point, where both gas and liquid become indistinguishable fluids, in which it exhibits properties of both liquid and gas. It is able to penetrate to solid like gas and dissolve other material into them like liquid. A higher molar ratio is required to push the reaction

forward in this method [121]. When this method was applied for production of biodiesel from crude Jatropha oil using methanol, a maximum conversion of 70% of Jatropha oil into fatty acids methyl esters was obtained in 10 minutes and the conversion continued increasing to 85% after 40 minutes under the same reaction conditions. The percentage of conversion was higher by around 2.5% when ethanol was employed under the same reaction condition [121, 122].

Latter in another study a 100% yield of methyl esters was obtained using supercritical method under milder conditions [123, 121]. The significant improvement is due to the free fatty acid (FFA) content in Jatropha oil. The FFA content of the Jatropha oil used in the latter study was only 2%, whereas the FFA content was more than 10% in the previous study. In a simpler explanation, higher FFA content will generate more water via esterification reaction, and thus, the water will hydrolyze the esters that produced from transesterification [121].

The main drawback of supercritical condition is that methyl/ethyl esters are easily degraded in an extremely high temperature (300 °C) [121].

4) Hydrogenation

Hydrogenation is a reductive chemical reaction that results in an addition of hydrogen (H_2), usually to saturate organic compounds. The process consists of the addition of hydrogen atoms to the double bonds of a molecule through the use of a catalyst [124]. Hydrogenated oil was found to have far better quality than fatty acid methyl ester (FAME), which is obtained from transesterification. Table 3.3 shows the comparison of chemical and physical properties of hydrogenated oil with FAME and EN 590 diesel (European diesel fuel standard).

Table3. 3: Chemical and Physical Properties of Hydrogenated oil, FAME and EN 590 Diesel [113]

Property	Hydrogenated oil	FAME	Diesel
Density at 15 °C [kg/m³]	775-785	885	835
Viscosity at 40 °C[mm²/s]	2.9-3.5	4.5	3.5
Cetane number	84-99	51	53
Sulphur content	~0	<10	<10

The cetane number of hydrogenated oil is very high, the storage stability is good and it has no content of sulfur, aromatics or ash. This gives benefits for the combustion process as well as for the catalytic after treatment processes. However, its density does not meet the European diesel fuel standard EN 590, but up to 30% can be blended into diesel still fulfilling the EN 590 norm [113].

B. Jatropha Biodiesel

The properties of biodiesel from Jatropha and its blends with petro diesel are in comparison with ASTM biodiesel standards. Because of high oxygen content, though the calorific value is a little lower than petro diesel, as a result, it helps in complete combustion.

An experimental data revealed that Jatropha biodiesel has a lower pour point, lower flash point, and a higher cetane number than soybean biodiesel, due to high concentration of saturated chains [125].

In fact, Jatropha oil has been highlighted as a potential biodiesel feedstock among the non-edible oils, because it has a higher cetane number as compared to diesel, which makes it a good alternative fuel that can be applied to conventional engine [126]

The quality of biodiesel is designated by several standards; like EN-14214 and ASTM D-6751, and the oxidation stability (OS) is among the monitored parameters as EN-14214 calls for determining oxidative stability at 110 °C with a minimum induction period (IP) of 6 hours by the Rancimat method (EN-14112), and ASTM standard D-6751 has recently introduced a minimum IP of 3 hours by same method. Indian specification IS-15607 also requires minimum induction time of 6 hours [127]. Table 3.4 gives the various properties of Jatropha biodiesel in varying blends with petroleum diesel [128] .

Table3. 4: Various properties of Jatropha biodiesel in varying blends with petroleum diesel [128]

S No.	Fuel blend	Density (kg/m ³)	Calorific value (kJ/kg)	Viscosity (cSt)	Flash point (°C)	Cloud point (°C)	Pour point (°C)
1	Diesel	850	44,000	2.87	76	6.5	3.1
2	JB20	852	43759.5	3.02	88	6.9	3.3
3	JB50	857	43,323	3.59	113	7.3	3.4
4	JB100	873	42,673	4.23	148	10.2	4.2

3.3.3.2. Seed Cake processing

Huge amount of seed cake would be left after the extraction of oil from Jatropha seeds for biodiesel production. The seed cake contains toxic materials like curcin and saponins, and thus is not suitable for animal feed. Further, if the seed cake is left open in the atmosphere, it would pollute the environment. Hence, to overcome this problem, proper utilization of seed cake is necessary. Production of biogas by anaerobic digestion could be one such possible solution to the above problem. In addition to this, the digested slurry can further be used as fertilizer in the fields [129]. It can also undergo pyrolysis to produce bio-oil, char and gas. The bio-oil or pyrolysis oil can further be upgraded to form green diesel. The details for

green diesel production from Jatropha seed cake has been given in Section 5.7.7 of Chapter 5, while for biogas and fertilizer uses it is given in the subsequent sub-sections.

A. Biogas Production

In an experiment, when Jatropha seed cake was anaerobically digested at different total solid contents (TS) and carbon to nitrogen (C:N) ratios in batch type digesters with 40 days hydraulic retention time (HRT), Biogas production from per kg of TS was found to be maximum i.e. 0.17 m³ at 20% TS of Jatropha seed cake slurry followed by 15%, 25% and 10% TS in that order as compared to 0.166 m³ in case of cow dung slurry alone. It was observed that when the carbon to nitrogen (C:N) ratio in the Jatropha seed cake slurry was between 22:1 to 27:1 (by adding different quantity of paddy straw) , higher gas was produced. Further, gas production from kg of TS of the mixture of Jatropha seed cake and cow dung was higher than that produced from Jatropha seed cake and cow dung slurry alone and was highest when Jatropha seed cake percentage in the mixture was within 25% [129].

B. Application as fertilizer

The seed cake of Jatropha, as well as the slurry left after anaerobic digestion of Jatropha seed cake, both contain nitrogen, phosphorous and potassium, and thus can be used as fertilizer for growing different crops. After anaerobic digestion, as a result of protein decomposition of the feedstock, the nitrogen content in the slurry increases by 5.9% as compared to seed cake, while phosphorous and potassium content remain the same. Thus, the fertilizer value, particularly nitrogen, increases in bio digested slurry because of lesser losses of nitrogen, as ammonia is available in the form of ammonium [129]. In an experiment it was found that both germination as well as growth of maize and potato plants was higher for treatments applied with Jatropha seed cake slurry as compared

to only soil. Moreover, the toxicity of Jatropha seed cake slurry, after anaerobic digestion, is lost and it can safely be applied as fertilizer for raising different crops [129].

3.3.4. End Combustion of Green diesel

Use of biodiesel in place of diesel lowers the emissions of unburned hydrocarbons, carbon dioxide, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, ozone-forming hydrocarbons, and particulate matter. Reductions in net carbon dioxide emissions are estimated at 77–104 g/MJ of petroleum diesel displaced by biodiesel. These reductions increase as the amount of biodiesel blended into the diesel fuel increases [38].

However, due to the higher temperature in the combustion chamber while using biodiesel, there is a slight increase in the NO_x (oxides of nitrogen) emissions. But there are antioxidants, which are quite effective in controlling NO_x formations. They do, however, have significantly more carbon monoxide and Hydrocarbon emissions. Among all the tested antioxidants p-phenylenediamine shows the best emission performance compared to biodiesel [26].

3.4. Concluding Remarks

It is very well clear from the current chapter that all the activities across the value chain of Jatropha, which are involved in production of green diesel require energy in some or the either form, for example fuel and electricity. Therefore, a viability study is required to find out the suitability of the crop as a green diesel feedstock. The viability indicators adopted in the current work are net energy balance and net energy ratio. This chapter, therefore, will form the base for the calculation of these viability indicators, later in Chapter number 5.