Biodiesel – Technologies and Business Opportunities

India, like many countries, has high hopes for Jatropha as a biofuel source, but little is known about how to make it a successful crop. **Bulk Agro (India) Pvt. Ltd.** digs for the roots of a new enthusiasm.

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INTRODUCTION:

The concept of bio fuel dates back to 1885 when Dr. Rudolf Diesel built the first diesel engine with the full intention of running it on vegetative source.

In 1912 he observed, " … *the use of vegetable oils for engine fuels may seem insignificant today. But such oils may in the course of time become as important as petroleum and the coal*

tar products of present time."

In 1970, scientists discovered that the viscosity of vegetable oils could be reduced by a simple chemical process and that it could perform as diesel fuel in modern engine. Since then the technical developments have come a long way and the plant oil today has been highly established as bio fuel, equivalent to diesel. Recent environmental *(e.g. Kyoto Protocol)* and economic concerns have prompted resurgence in the use of biodiesel throughout the world.

In 1991, the European Community proposed a 90% tax reduction for the use of bio fuels, including biodiesel. Today 21 countries worldwide produce biodiesel. India is one of the largest petroleum consuming and importing countries. India imports about 70 % of its petroleum demands. The current yearly consumption of diesel oil in India is approximately 40 million tones constituting about 40% of the total petro-product consumption.

Why Biodiesel?

Biodiesel, derived from the oils and fats of plants like *sunflower, rape seeds, Canola or Jatropha Curcas*, can be used as a substitute or an additive to diesel. As an alternative fuel biodiesel can provide power similar to conventional diesel fuel and thus can be used in diesel engines. Biodiesel is a renewable liquid fuel that can be produced locally thus helping reduce the country's dependence on imported crude.

The advantages of biodiesel are enumerated hereunder :

 Biodiesel is non toxic & environmental friendly as it produces substantially less carbon monoxide and 100% less sulfur dioxide emissions with no unburnt hydrocarbons and thus it is ideal fuel for heavily polluted cities. Biodiesel reduces serious air pollutants such as particulates and air toxicity.

 Due to its less polluting combustion, biodiesel provides a 90% reduction in cancer risks and neonatal defects.

 Biodiesel is biodegradable and renewable by nature.

 Biodiesel can be used alone or mixed in any ratio with conventional diesel. The preferred ratio of mixture ranges between 5 and 20%

 Biodiesel extends the life of diesel engines.

 Biodiesel could be cheaper than conventional diesel.

 Biodiesel has good potential for rural employment generation.

Biodiesel : Common Plant Sources

Under Indian conditions such plants varieties, which are non-edible and which can be grown abundantly in large-scale on wastelands, can be considered for biodiesel production. Some of the prominent non-edible oil seed producing plants include *jatropha curcas or ratanjyot, pongamia pinnata or karanj, calophyllum inophyllum or nagchampa, hevea brasiliensis of rubber seeds, calotropis gigantia or ark, euphorbia tirucalli or sher, boswellia ovalifololata, neem* etc.

Selection of Species : *Jatropha Curcas*

Considering all the options available among non-edible Tree Bearing Oil (TBO) seeds, *Jatropha Curcas* has been identified as the most suitable seed. Jatropha is a genus of approximately 175 succulents, shrubs and trees from the family Euphorbiaceae. Plants from the genus are natives of Africa, North America and the Caribbean. Originating in the Caribbean, the Jatropha had spread as a valuable hedge plant to Africa, Asia and to India by Portuguese traders. Jatropha Curcas is a widely occurring variety of TBO. It grows practically all over India under a variety of agro climatic conditions. Thus it ensures a reasonable production of seeds with very little inputs.

Jatropha : The Preferred Option

The advantages of the specie are as follows :

· Jatropha can be grown in arid zones (20 cm rainfall) as well as in higher rainfall zones and even on land with thin soil cover.

· It is a quick yielding specie even in adverse land situations viz. degraded and barren lands under forest and non-forest use, dry and drought prone areas, marginal lands, even on alkaline soils and also as agro-forestry crops. Jatropha can be a good plantation material for eco-restoration in all types of wasteland.

· Jatropha grows readily from plant cuttings or seeds up to the height of 3 - 5 m.

· Jatropha is not considered good forage material.

· The plant is highly pest and disease resistant.

· Various parts of the plant are of medicinal value, its bark contains tannin, the flowers attract bees and thus the plant is honey production potential.

· Jatropha removes carbon from the atmosphere, stores it in the woody tissues and assists in the build up of soil carbon.

3.1.2 _Jatropha :_ The Limitations

The Jatropha also suffers from certain limiting factors, which need to be kept in mind while dealing with the specie. These are as follows:

 Jatropha cannot be grown on waterlogged lands and slopes exceeding 30o.

 The ideal climatic conditions for Jatropha can be summarized as annual rainfall not exceeding 600 mm in moderate climatic conditions, 1200 mm in hot climatic zones and soil pH less than 9. The atmospheric temp. should not fall below 0o C as the plants are sensitive to ground frost that may occur in winters.

 Jatropha seeds are hard and possess toxicity

 The golden flea beetle *(Podagrica spp.)* can harm particularly on young plants.

 Jatropha is also host to the fungus *"frogeye" (Cercospera spp.),* common in tobacco

Jatropha Cultivation : Yield and Productivity

Apart from planting the seeds, Jatropha can also be propagated vegetative from cuttings. Use of branch cutting for propagation results in rapid growth and the bush can be expected to bear fruit within one year. Seeds are best sown during mid-February to mid-March and the seedlings 60-75 cms. tall can be transplanted to the field. The ideal planting pitch has been found to be 2m x 2m thus resulting in 2500 plants per hectare. Wider spacing would give larger yields of fruit @794 Kgs/ha. Like all perennial plants, Jatropha displays vigorous growth in youth that tails off gradually towards maturity. In equatorial regions where moisture is not a limiting factor (i.e. continuously wet tropics or under irrigation), Jatropha can bloom and produce fruit throughout the year. To withstand extreme drought conditions, Jatropha plant sheds leaves to conserve moisture, which results in reduced growth. Although Jatropha is adapted to soils with low fertility and alkalinity, better yields can be obtained on poor quality soils if fertilizers containing small amounts of nutrients viz. *calcium, magnesium* and *sulfur* are used for the first two years. Jatropha plant bears fruits from 2nd year of its plantation and the economic yield stabilizes from 4th or 5th year onwards. The plant has an average life with effective yield up to 50 years. Jatropha gives about 2 Kgs. of seed per plant. In relatively poor soils such as in Kutch (Gujarat), the yields have been reported to be 1 Kg per plant while in lateritic soils of Nasik (Maharashtra), the seed yields have been reported as **0.75 -** 1.00 Kg per plant. Thus the economic yield can be considered as 0.75-2.00 Kgs./plant and 4.00-6.00 MT per hectare per year depending on agro-climactic zone and agricultural practices. One hectare of plantation on average soil will give 1.6 MT oil. Plantation on poorer soils will give 0.9 MT of oil per hectare. The cost of plantation has been estimated as Rs.20,000/- per hectare, inclusive of plant material, maintenance for one year, training, overheads etc. It includes elements such as site preparation, digging of pits, fertilizers, irrigation, deweeding, and plant protection for one year i.e., the stage when it will start bearing fruits.

Jatropha to Biodiesel : Process Steps

1) Preparation of Seeds

The ripe fruits are plucked from the trees and the seeds are sun dried. They are decorticated manually or by decorticator. To prepare the seeds for oil extraction, they should be solar heated for several hours or roasted for 10 minutes. The seeds should not be overheated. The process breaks down the cells containing the oil and eases the oil flow. The heat also liquefies the oil, which improves the extraction process. Oil can be extracted from the seeds by heat, solvents or by pressure. Extraction by heat is not used commercially for vegetable oils. The oil from Jatropha seeds can be extracted by three different methods. These are *mechanical extraction* using a screw press, *solvent extraction* and an intermittent extraction technique viz. *soxhlet extraction*.

2) Purification of Oil

The oil extracted as above can be purified by the following means:

Sedimentation

This is the easiest way to get clear oil, but it takes about a week until the sediment is reduced to 20 - 25 % of the raw oil volume.

Boiling with water

The purification process can be accelerated tremendously by boiling the oil with about 20 % of water. The boiling should continue until the water has completely evaporated (no bubbles of water vapour anymore). After a few hours the oil then becomes clear.

Filtration

Filtration of raw oil is a very slow process and has no advantage in respect of sedimentation. It is not recommended.

4.3 Processing of Oil

The quality of feed vegetable oil particularly FFA content plays an important role in identifying the suitable technology. The important factors to be considered for a biodiesel production plant include:

- Process ability of variety of vegetable oils without or minimum modifications
- Process ability of high free fatty acid (FFA) containing oils/feed-stocks
- Must be able to process raw both expelled and refined oil
- Process should be environment friendly with almost zero effluent

Certain difficulties are experienced in IC engines while using straight vegetable oil (SVO) or chemically unmodified vegetable oils. One major problem is the higher viscosity of vegetable oils. The triglycerals as present in vegetable oil are mostly associated with their high viscosities, low volatilities and polyunsaturated character. Thus property modifications by trans-esterification are required to impart properties similar to petroleum diesel to the vegetable oil. The selection of appropriate technology for production of biodiesel calls for careful selection of processing steps, catalyst and downstream process integration.

Various methods for processing of oil are as follows:

· Pyrolysis
· Micro-emulsification
· Trans-esterification

Pyrolysis

Pyrolysis refers to a chemical change caused by application of thermal energy in absence of air or nitrogen. The liquid fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. The pyrolyzate has lower viscosity, flash & pour points than diesel fuel but equivalent calorific values. The cetane number of the pyrolyzate is lower. The pyrolysed vegetable oils contain acceptable amounts of sulphur, water and sediment with acceptable copper corrosion values but unacceptable ash, carbon residue and pour point.

Micro-emulsification

The formation of micro-emulsions (co-solvency) is a potential solution for reducing the viscosity of vegetable oil. Micro-emulsions are defined as transparent, thermodynamically stable colloidal dispersions. The droplet dia. in micro-emulsions ranges from 100 to 1000 Å. A micro-emulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, an alcohol and a surfactant and a cetane improver, with or without diesel fuels. Water (from aqueous ethanol) may also be present in order to use lower-proof ethanol, thus increasing water tolerance of the micro-emulsions.

4.3.3 Transesterification

The process of converting the raw vegetable oil into biodiesel, which is fatty acid alkyl ester, is termed as transesterification. There are three basic routes to biodiesel production from biolipids (biological oils and fats) :

 Base catalyzed transesterification of the biolipid carried out under atmospheric pressure and at temperature ~60-70o C

· Direct acid catalyzed transesterification of the biolipid

· Conversion of the biolipid to its fatty acids and then to biodiesel

The processing steps for the most commonly used method viz. base catalyzed transesterification of the biolipid would be as follows :

1. Exact quantity of potassium hydroxide required as determined by titration is thoroughly mixed in methanol till it dissolves completely to result in potassium methoxide.
2. Jatropha oil is heated, if required (during winter), and mixed in the potassium methoxide while with agitator running.
3. It is then allowed to settle and glycerine is removed from bottom.
4. Biodiesel fraction is then washed and dried.
5. It is then checked for quality.

Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis. Methanol is most commonly used for the purpose since it is the cheapest alcohol available. Ethanol and higher alcohols such as isopropanol, butanol etc. can also be used for the esterification. Using higher molecular weight alcohols improves the cold flow properties of biodiesel but reduces the efficiency of transesterification process.

The reaction is as follows :

Methods commonly used for producing biodiesel are batch and continuous processes. In general, smaller capacity plants and variable feedstock quality warrant use of batch systems. Continuous systems generally lead the operation on a 24x7 basis, requiring larger capacities to justify larger staffing needs and also requiring uniform feedstock quality. The transesterification works well when the input oil is of high quality. However, quite often low quality oils are used as raw materials for bio-diesel preparation. In cases where FFA content of the oil is above 1%, difficulties arise due to the formation of soap, which promotes emulsification during the water washing stage. If the FFA content is above 2%, the process becomes unworkable.

The factors affecting the transesterification process are i) oil temp. (ii) reaction temp. (iii) ratio of alcohol to oil (iv) catalyst type & conc. (v) intensity of mixing (vi) purity of reactants

The approx. process constituents are listed hereunder :
Vegetable oil Alcohol Catalyst (Sodium or Potassium Hydroxide)
Glycerin Bio-diesel
100 gm 12 gm 1 gm 11 gm 95 gm

Transesterification *: Industrial Practice - Lurgi Process*

Lurgi's process of transesterification is used most widely in the world. The process involves intensive mixing of methanol with the oil in presence of a catalyst, and then separation of lighter methyl ester phase by gravity from the heavier glycerol. The process flow chart for production of biodiesel is illustrated in Figure below. Oil, methanol and sodium methylate catalyst are mixed in the reactor (R-I) and allowed to separate into two phases. The lighter methyl ester/oil phase is mixed with additional methanol and catalyst in the reactor (R-II) followed by gravity separation. This second reactor stage maximizes the biodiesel yield and quality. The lighter phase is washed with water to remove residual glycerol or methanol dissolved in the ester phase, followed by vacuum drying to yield biodiesel. The denser glycerol phase from R-II containing excess methanol and catalyst is recycled to the front end of R-I. The denser glycerol phase leaving R-I still containing excess methanol is distilled for its recovery in the Methanol Recovery Column and sent back to R-I. The wash water from the Water Wash Column is used in the Methanol Recovery Column. Thus the entire methanol is consumed in the production of methyl ester. The heavier fraction from the Methanol Recovery Column is processed in the Glycerin Water Evaporation Column to recover crude glycerin (conc. 80-85%) as a byproduct. This can be further upgraded to pharmaceutical glycerin by distillation, bleaching, if required, and vacuum drying.

The key features of Lurgi's biodiesel process are:

- Technology applicable to multiple feedstock
- Continuous process at atmospheric pressure and at 60°C
- Dual Reactor System operating with a patented Glycerin Cross Flow configuration for maximized conversion
- Recovery & recycling of methanol
- Closed loop water wash recycle to minimize waste water
- Phase separation by gravity process (no centrifuges necessary)

Almost all the biodiesel is produced using the base catalyzed transesterification process as it is the most economical one requiring only low temperatures & pressures with 98% yield. Other processes under development include *biocatalyzed transesterification, pyrolysis of vegetable oil/seeds and transesterification in supercritical methanol*.

Transesterification : Critical Issues

- Interference of FFA with transesterification deactivates the basic catalyst resulting in loss of catalyst and biodiesel yield.
- As water content of the oil deactivates catalysts, drying of oil may be required.
- Soaps formed with basic catalyst is difficult to remove.

Biodiesel: Physical Characteristics

Properties Values

Specific gravity 0.87 to 0.89

Kinematic viscosity@ 40°C 3.7 to 5.8

Cetane number 46 to 70

Higher heating value (Btu/lb) 16,928 - 17,996

Lower heating value (Btu/lb) 15,700 - 16,735

Sulphur wt % 0.00 - 0.0024

Cloud point °C -11 to 16

Pour point °C -15 to 13

Iodine number 60 - 135

Storage of Biodiesel : Problems Encountered

The efficient storage of biodiesel resources can provide energy security to the country. Adequate data are not available for long-term storage of biodiesel and blends. Based on the experience, biodiesel can be stored up to a max. 6 months.

As a mild solvent, biodiesel tends to dissolve sediments normally encountered in old diesel storage tanks. Brass, Teflon, lead, tin, copper, zinc etc. oxidize biodiesel and create sediments. The existing storage facilities and infrastructure for petrol & diesel can be used for the biodiesel with minor alterations. For biodiesel storage, shelf life and how it might break down under extreme conditions assume importance.

The following merit attention for storage of biodiesel :

- Biodiesel has poor oxidation stability. Use of oxidation stability additives is necessary to address this problem.
- Low temperature can cause biodiesel to gel, but on warming it liquefies quickly. Hence, insulation/jacketing of storage tanks and pipelines would need to be done at the low temperature zones.
- To avoid oxidation and sedimentation of tanks with biodiesel, storage tanks made of aluminum, steel etc. are recommended for usage.

Indian Scenario

There has been greater awareness on biodiesel in India in the recent times and significant activities have picked up for its production especially with a view to boost the rural economy. The activities launched in the field of bio-diesel in India and the agencies involved therein include:

· Development of high quality Jatropha through tissue culture.

· Plantation by National Oilseed and Vegetable Oil Development Board (NOVOD), NAEB, NGOs & private companies

· Pilot plants for biodiesel production

· Trans-esterification plants with capacities : 300 MT/day & 30 MT/day in AP, 5.00 MT/day

· Supply of biodiesel.

A National Mission on biodiesel has been proposed by the Govt. of India comprising six micro-missions covering the essential aspects of plantation, seed procurement, oil extraction, transesterification, blending & trade and R&D. Indian Oil has worked on establishing the production parameters of transesterified Jatropha oil and use of biodiesel in its R&D Centre at Faridabad. They have been using a laboratory scale plant of 100 Kgs./day capacity for
transesterification; designing of larger capacity plants is underway. Production of biodiesel in smaller plants of capacity e.g. 5-20 Kgs./day may also be started in villages. Substantial developmental activities have been carried out in regard to the production of biodiesel through transesterified non-edible oil has worked on marginally altering the engine parameters to suit the Indian Jatropha seeds and to minimize the cost of transesterification process.

Oil Seed Crushing and Oil Extraction : Current Status

Presently the edible oil is extracted through traditional *ghani*. The recovery of oil in the *ghani* is lesser and of inferior quality. The capacity is also much less as compared to the improved expellers. Oil extraction can be more effectively carried out by the following methods:

Method 1: Prepressing of seeds lightly can precede oil milling. This results in higher capacity; lower power consumption, lower wear & tear and maintenance. The oil recovery is lower in this case.

Method 2: Here either in the same screw press – two-stage pressing is carried out or prepressed cake from first stage screw press in sent for second pressing to other screw press. Any kind of oil-bearing seed can be processed in oil mill, preparatory equipments are recommended prior to expelling. Pressed cake can be sold after
recovering the max. oil. Hence, double pressing system is recommended. Depending on process sophistication, the cost of oil extraction will be 19-90 paise per litre.

The disadvantages of expellers are listed as follows :

- The press must operate continuously for at least eight hours; intermittent operation is unsatisfactory.
- Oil from an expeller contains more impurities than oil from a batch press and must be filtered to obtain clean oil.
- Maintenance costs are high and it requires skilled mechanics.

Commercial Production of Biodiesel : Indian Efforts

In India, approximate 85% of the operating cost of biodiesel plant is the cost to acquire feedstock. Securing own feedstock to insure supply at a fair price and sourcing it locally to avoid long haulage for delivery of seeds to biodiesel plant are critical factors in controlling profitability.

The capital cost both in India and internationally are ~Rs.15,000 - 20,000/- per MT of biodiesel produced. At 10000 MTPA, the capital cost of oil extraction and transesterification plant would be Rs.20,000/MT capacity. A plant size of **10,000 MTPA** can be considered optimal assuming cost of oil extraction at Rs.2360/MT and cost of transesterification at Rs.6670/MT with by-products produced @ 2.23 MT seed cake/MT of biodiesel and 95Kgs. of glycerol per MT of biodiesel. Fixed costs towards manpower, overheads & maintenance is 6% of capital cost, depreciation is 6.67% of capital cost. The return on investment (ROI) is 15% pretax on capital cost.

Conclusion

Production of bio-fuel from plant materials is a major step toward harnessing one of the world's most-prevalent, yet least-utilized renewable energy resources. A breakthrough process for converting biomass into biodiesel fuel promises a cheaper way to go green. Eco-dreamers have long been hoping for a way to mitigating the global warming, but the slow pace of progress in alternative fuel technologies has prevented that vision from materializing. Ethanol, the most popular and commercial biofuel, has long been refined out of plant matter, but it requires the costly, energy intensive step of distilling every molecule of water out of the solution. In contrast, the biodiesel process is based on aqueous phase reactions, which does not to go through the expensive distillation phase. As the process is exothermic, there is no need for distillation which need a lot of energy. The resulting biodiesel has almost the same chemical structure as traditional diesel and burns the same way in diesel engines.

The leading oil companies in the world are currently looking forward to tap the excellent business opportunity offered by biodiesel. If the developed process is scaled up to commercial levels by more and more oil companies, it could be a major step towards the creation of an eco-friendly transportation fuel that is relatively clean on combustion and provides farmers with substantial income. The technologies available for biological conversion of cellulosic biomass to biodiesel enjoy a high potential to succeed in the commercial marketplace. India, with its huge waste/non-fertile lands, has taken a well noted lead in the area and commercial production is where the industries have to focus on for self sustainable development. India’s biodiesel programme has been based on Jatropha seeds only but for reduced operating cost a multiple feedstock-based strategy is needed.