

**UNDERSTANDING THE BIO-
DIESEL TECHNOLOGIES FROM
“CONCEPT TO CLARITY”**

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Introduction:

What are bio-fuels?

Bio-fuels are liquid or gaseous fuel made from plant materials and/or residues such as, agricultural crops, municipal wastes and agricultural and forestry by-products. Bio fuels can substitute conventional fuels in vehicle engines-either totally or partially in a blend. The major types of bio-fuels and their conversion technology are briefly described below.

- **Bio-ethanol:** – is mainly produced by fermentation from grains rich in sugars or starch, for example, cereal crops, sugar beet and sorghum plants. It is blended with conventional petrol, usually, at 5% additives and can be used in modern spark-ignition engines without modifications.
- **ETBE:** - (Ethyl-tertiary-butyl-ether) is produced from the bioethanol by reaction with isobutylene. ETBE is used as a fuel blend up to 15% with conventional petrol. Ethanol and ETBE, share the advantage of being high-octane product.
- **Bio-diesel:** - is mainly produced from oil crops, waste oils, animal fats etc. by transesterification process. Bio-diesel is used in compression-ignition diesel engines, usually, 5% blend in the car and up to 30% blend in “captive fleet” such as a city buses.
- **Biogas:** - this results from the anaerobic fermentation of organic matter to produce a mixture of methane (60%) and carbon dioxide. Organic matter such as livestock manure, food –processing residues as well as municipal sewage sludge is used as raw material to produce biogas in dedicated reactors.
- **Bio-fuels from woody materials:** - bio-ethanol is currently produced from energy crops that are rich in sugars and starches. However, plants are mainly composed of lignin and cellulose and not starches. It is difficult to convert cellulose to bio-ethanol but current research aims to solve this problems.

However, this paper would focus mainly on bio-diesel technology and related issues

The bio-diesel is a fuel consisting of long-chain fatty acid alkyl esters made from renewable vegetable oils, recycled cooking greases, or animal fats “that meets ASTM & EN standards

A Bio-fuel with properties similar to No. 2 petroleum diesel fuel

An important characteristic of diesel fuel is its ability to ignite on its own, as it must in a diesel engine. This ability is quantified by the fuel’s cetane number, where a higher cetane number means that the fuel ignites more quickly.

Bio-diesel properties:

	Bio-diesel	Diesel
Molecular weight (kg/kg mol)	296	170-200
Cetane number	50-52	47-50
Density (kg/l) @ 15 °C	0.88	0.84
Lower calorific value (MJ/kg) @ 15 °C	37.3	42.7
Air/fuel ratio (kg air/kg fuel)	12.3	14.53
Oxygen content (wt%)	9.2-11	0-0.6
Kinematic Viscosity mm ² /s @ 20 °C	7.4	4
Flash Point °C	95-135	77

As we can see that the viscosity of bio-diesel is still about twice the value of diesel, which affects the atomisation of the fuel during the injections. Below temperature of zero degree, problem can occur with the supply of fuel from the tank to the engine and cold start of the engine. These problems can be addressed by fuel heating or adding additives like flow enhancers.

The table indicates a higher cetane number of bio-diesel as compared to regular diesel. This denotes a good ignition quality, which leads to a higher engine efficiency and emission reduction. The stoichiometric air/fuel ratio is somewhat lower for bio-diesel, which indicates that less air is needed to burn the same quantity of fuel. The density of bio-diesel is somewhat higher than that of diesel. This higher density compensates for reduced energy content (Gravimetric calorific value) of bio-diesel to some extent. Because vehicle-using bio-diesel have, on an energy basis, the same fuel consumption as those running on diesel fuel, this lower energy content leads to higher fuel consumption.

The bio-diesel, however, differs from regular diesel with respect to some properties that are not directly related to the engine performance. One of them is the fuel flash point, which is primarily important for the safe handling of the fuel.

In connection to directive 2003/30, two fuels standard support the market implementation of bio-diesel.

- a) **The European standard for bio-diesel “ EN14214 Automotive fuels- Fatty acid methyl esters (FAME) for diesel engines”** came into force in 2004. The 25 parameters defined within EN 14214 represent currently the strictest standard for bio-diesel worldwide. Further on, this standard is neutral to the type of feedstock used and therefore opens the markets besides rapeseed oil to other types of oils and fats.
- b) **EN590 Automotive fuels – Diesel (2004)”** allows blending of mineral diesel with up to 5% FAME EN 14214 resulting in a bio-diesel market potential within the EU of more than 6 millions tons per year.

Bio-diesel terminology:

Pure biodiesel or 100% Biodiesel is termed as B100

Bio-diesel Blends are classified as follows;

- BXX for XX% bio-diesel
- B20 is 20% bio-diesel and 80% petrol diesel fuel
- B5 is 5% bio-diesel and 95% petrol- diesel fuel

Thus it is important to avoid calling blends as “bio-diesel” because it can lead to a lot of confusion! – What is true for B100 may not be true for B20 and visa versa

By several measures, blends of bio-diesel and petroleum diesel perform better than petroleum diesel alone, but the relatively high production costs of bio-diesel and the limited availability of some of the raw materials used in its production continue to limit its commercial application.

WHY PRODUCE BIODIESEL?

Important characteristic of biodiesel is lubricity. Fuel injectors and some types of fuel pumps rely on fuel for lubrication. Bio-diesel has better lubricity than low-sulphur petroleum diesel or the ultra-low-sulphur petroleum diesel to be introduced in 2006. As per the norms set, Diesel fuel must lower sulphur content from 500ppm to below 5ppm starting 2006. Sulphur is the lubricity component of diesel fuel and will need a substitute. 1% bio-diesel can improve the lubricity of low sulphur diesel fuel by 40%.

At Kyoto, the EU committed itself to an 8% reduction in annual green house gas emission by 2010 compared with the 1990 level.

Various studies have estimated that the use of 1 kg of biodiesel leads to the reduction of 3 kg of CO₂. Biodiesel is low in sulphur and has a fast biodegradability. Transport produces 28% of Europe's Carbon Dioxide and road transport will account for 90%. So implementing substitute fuels that reduce CO₂ emissions is vital to meet the Kyoto Protocol commitments.

The competitiveness of bio-diesel to fossil diesel depends on the fuel taxation approaches and levels. Bio-diesel is not competitive to fossil diesel where the positive externalities such as impacts on environment, employment, climate changes and trade balance are not reflected in the price mechanism.

In Europe, fixed incentive is the key instrument to enhance the biodiesel as an alternative fuel for transport.

Feed-stock for Bio-diesel Production:

Based on actual political framework, selling biodiesel is not an issue any more and the major limiting factor is, therefore, a sourcing of cost effective feedstock. Thus developing a successful bio-diesel project has, besides the selection of the proper technology, mainly to focus on the development of feedstock supply.

Traditional raw materials for bio-diesel production are rapeseed oil (current market share about 85%), sunflower oil, soybean oil and palm oil. Besides these types, animal fats and used cooking oils are major interest for bio-diesel production as the prices are only half as compared to fresh vegetable oils.

Another way of reducing production cost and come along with limited local resources of vegetable oils is the use of non-edible oils for bio-diesel fuels. The various investigations has now proved that jatpropha oil, whose fatty acid analysis shows that it resembles with fatty acid composition of rapeseed oil, methyl esters had brought promising results.

Further on a number of non-edible vegetable oils of Indian origin might be suitable as low cost feedstock for bio-diesel production. It is estimated that potential of such oils in India amounts to about 1 million tons per year.

PRODUCTION OF BIODIESEL FROM MULTIFEED STOCK.

The production process can be divided into the following main process steps.

Oil-pretreatment:

Prior to main process of trans-esterification, vegetable oils usually have to undergo a number of refining and/or pretreatment steps as summarized below:

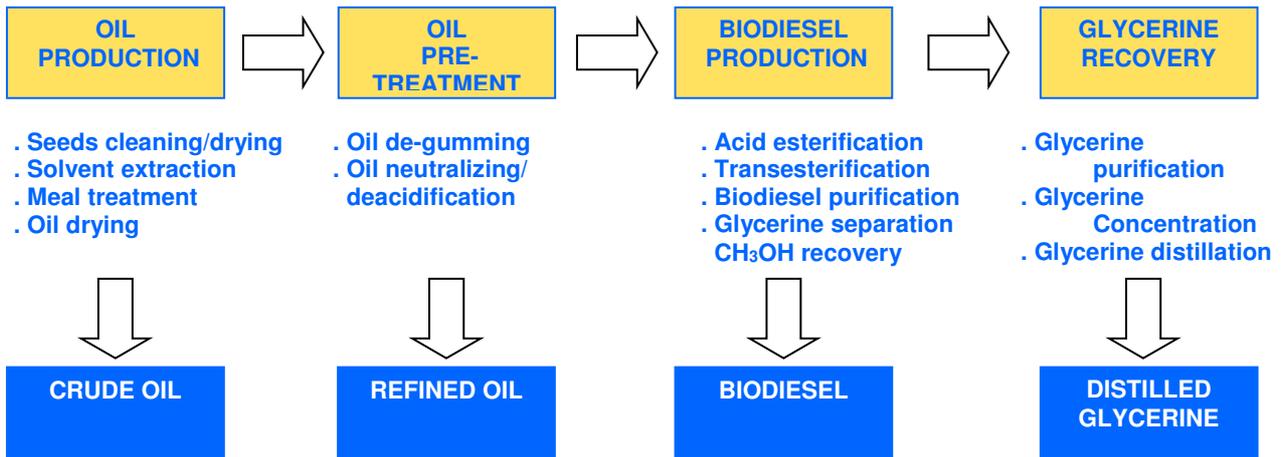
The main purpose of is to Minimize subsequent process losses, catalyst and methanol consumption, and another objective is to Maximize product quality through; Moisture control (< 0.1%), Cloud point control (< 5°C), Free fatty acid control (<0.2%), Phosphorus control (< 10 ppm) prior to transesterification.

The various pre-treatment techniques used are;

- Acid degumming to reduce phosphorus
- Chemical refining to reduce FFA & phosphorus
- Physical refining to reduce FFA
- Vacuum drying to reduce moisture
- Winterising / Fractionation to reduce cloud & melting point
- Esterification to convert FFA to biodiesel FAME

The overall technological scheme offered is for the production of Biodiesel and Glycerine starting from seeds and/or crude/neutral and/or refined vegetable oils is summarised here below:

DESMET BALLESTRA BIODIESEL TECHNOLOGY



A "transesterification" is the conversion (switching) of one ester into another -- a glyceride ester into an alkyl ester in the case of biodiesel, where methanol (or ethanol) replaces the glycerine.

An "esterification" is the conversion of a non-ester into an ester. FFAs are non-esters. FFAs are converted into esters by acid esterification in the first stage of the two-stage acid-base biodiesel process, but cannot be converted by the more common single-stage base transesterification process. Here the FFAs must be removed from the process, or they will dissolve in the biodiesel being formed, yielding an acidic, poor-quality fuel that will not meet quality standards.

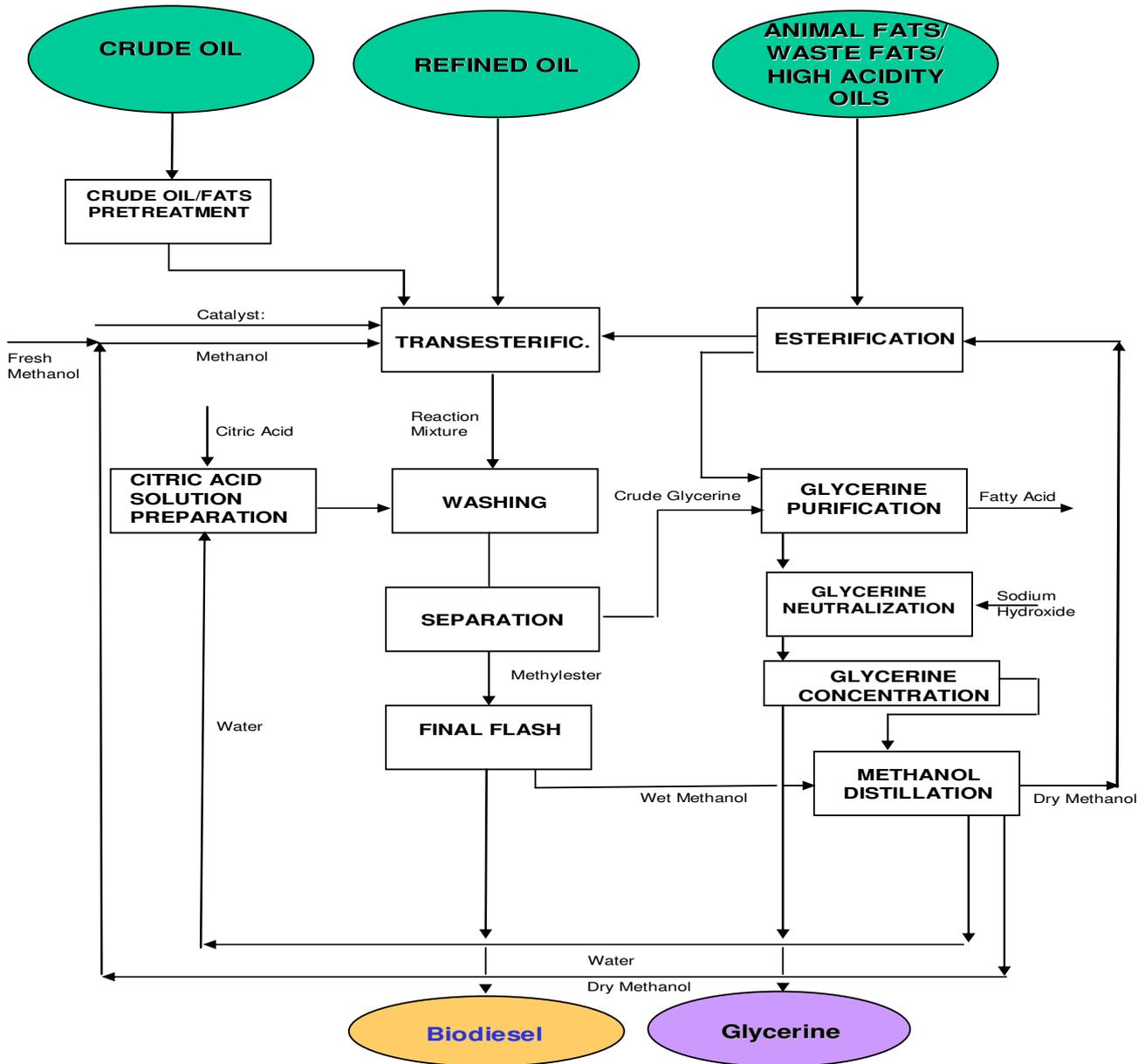
The basic sodium methoxide quantity used in transesterification acts as a catalyst, not a neutralizer. Lye attacks ester bonds, breaking the bond, and the alcohol drops off, leaving an open-ended fatty acid chain. With glycerides the alcohol that drops off is glycerine. The affinity of the replacement methanol or ethanol for the resulting open bond is strong enough to prevent the glycerine reattaching to the fatty acid.

This is also why it is critical that a minimal amount of catalyst is used, as it will continue to attack ester bonds, even those of biodiesel. Too much lye/catalyst will break the biodiesel ester bonds; some of the broken bonds will mate with the lye/catalyst and form excess soap, and others will match up with a water molecule to form FFAs, which dissolve back into the biodiesel. It is this excessive formation of FFAs that the "acid number" in the US ASTM and other national quality standards refers to.

While it is unavoidable that some FFAs are formed by biodiesel ester bonds being broken, excess lye increases the proportion.

The Biodiesel production section, namely the Transesterification of Oils and the Biodiesel Purification step are characterised by unique features that with reference to the illustrated Process Block Diagram, are here below described:

BIODIESEL PRODUCTION PLANT



The transesterification reaction is accomplished in 3 steps with a methanol surplus with respect to the stoichiometric quantity, using an alkali methylate in anhydrous methanol solution as a catalyst.

Methanol and catalyst are dosed and recycled to the 3 reaction steps within prefixed rates.

Reaction temperatures are lower than 60°C and pressure is max 0,5 bar(g). Overall residence time of the whole plant is 2 hours approx.

The yield of the continuous transesterification is 99,8% calculated as ratio of Neutral / Refined Oil fed to the transesterification versus the produced Biodiesel

At the end of the transesterification process, two phases are accurately separated.

Purification of the upper methyl ester phase involves separation of un-reacted methanol, washing with water solutions and final drying.

Purification of the lower glycerine phase involves: splitting of soaps and separation of fatty matter, neutralisation, separation of un-reacted methanol, dilution with wash liquid stream coming from methyl ester washing, splitting of soaps and final concentration up to 88 - 90%.

Partially refined glycerin can be delivered as such or sent to the upgrading-distillation section up to pharmaceutical grade meeting the most stringent pharmacopoeia specifications.

These operations are performed by means of process sequence and equipment characterized by:

- Mild operating conditions
- Completely Computerized Process Control System
- Simple mechanical design of the process equipment and negligible maintenance demand
- Small overall dimensions of the Units and equipment

In particular the Transesterification step entails these peculiarities:

- Continuous operation-mode with multiple glycerin separation for each single step
- Enhanced reactor Kinetics due to the "Solvation" effect of the excess Methanol vs. the quantity of oil to be reacted
- Limited product hold-up
- Operation flexibility deriving from the possibility to dose the reactants to the 3 steps in variable and specifically pre-set quantities
- Possibility to process oils of widely variable quality and origin
- Easy and accurate control of the process key-parameters (temperatures pressures and flow rates)

When accounting for the kinetics aspects of the transesterification reaction, a continuous process shows peculiar advantages with respect to the traditional batch process, as here below detailed:

The initial step of the reaction consists in the solvation of the oil molecules by the excess reactant (methanol); this step is slow, due to the scarce affinity between the two reactants and is accelerated by the presence of methyl ester that, being a mutual solvent, acts as a **“phase transfer agent”**.

In a batch system, where no methyl ester is initially present in the reaction mixture, the transesterification reaction requires, therefore, a dwell time before appreciable amount of methyl ester are produced. Conversely, in a continuous process, the two reactants are fed to a reaction mixture containing the steady state methyl ester amount, and the resulting fast contact between the two reactants enhances the overall kinetics.

An almost tenfold viscosity reduction is observed when oil is converted to methyl ester; the steady state viscosity of a continuous reactor is, therefore, consistently lower than the initial reaction mixture viscosity of a batch system, which allows an overall higher mixing intensity at comparable mixing energy inputs.

The above aspects add up to the general advantages of a continuous process (reduced equipment sizes at given plant capacity thanks to the elimination of loading/unloading dead times, reduced energy and utilities consumption, easier automation of process control, higher product quality uniformity), making it almost a must, once the economics of a commercial scale plant are accounted for.

As for the plant safety management, the reduced reaction volumes imply that much lower methanol amounts are present at any time in the process sections, which greatly reduces the fire hazard.

A further feature, unique to the DB continuous process, resides in the dedicated reactors design, which allows the continuous separation of the glycerin phase from the reaction mixture within each of the three reaction steps. This allows shifting the reaction equilibrium toward the products, so maximizing the yield, and to minimize the catalyst consumption.

As for the downstream Methyl ester purification unit, the DB technology foresees the following steps:

- Evaporation (BEFORE the Methyl ester washing section) of most (85% approx.) of the un-reacted methanol in dry form, suitable for direct recycle to the transesterification section.
- Washing of the residual glycerin and soaps by means of water; the water phase leaving from this section is recycled to the glycerin purification section
- Final Methyl ester drying; the wet methanol stream separated in this section is sent to a rectification unit, in order to recover it to the transesterification section.

CRITICAL ANALYSIS: SELECTION OF CHEMICALS, FEEDSTOCK AND THE PROCESS:

Feed stock selection and quality aspect:

a) Type of oil: The process works on all kinds of tryglycerides, but some characteristics of the ester are directly links to the kind of oil. The quality specifications of bio-diesel of (B100) are well described in various national and international standards. E.g. Iodine value, are strictly related to the type of feed stock, while others can be influenced by the pre-treatment of the oil/fats (sulphur, phosphorous content), the trans-esterification itself, (ester content, acid value, MG, DG, and TG content) or any post-treatment of the bio-diesel e.g. Improvement of the CFPP by addition of cold flow improvers)

Besides quality, the bio-diesel yield is also an important aspect of the bio-diesel process. Bio-diesel or fatty acid methyl ester (FAME) yield, as well as, methanol consumption, water/glycerol production depends upon the nature and the composition of the feedstock.

This means that BD yield is feed stock-dependent and that parameters like average relative molecular mass, FFA, and partial glycerides content must be analyzed to asses the nature of the feed stock for BD production.

b) FFA – Content: High FFA means high catalyst consumption and high soap content. Free fatty acids do not participate in the trans-esterification reaction, but they are the culprit of huge catalyst consumption and at the end they re-appear as fatty acid.

As the soap formed are in the glycerol phase after the decantation more acid will be needed to split the soap in to fatty acid and water. Finally, more catalyst and more acids mean more salt in the final glycerol and the deterioration of the quality.

Thus the best results will be obtained when FFA content is well below 0.2%...

c) "P" content: Forming emulsions is the job they will do if there is too much 'P' content in the oil. In practice, the emulsion will be present as a in between layer in the decanter after trans-esterification. This layer is to be taken to the glycerol treatment where the contact with acid will split the emulsion in ester and glycerol. Finally this ester will be found in the fatty acid phase, so that too high 'P' content will result in a loss of ester, bringing down the BD yield and also the deterioration of the fatty acid quality.

Thus experience in several plants shows that a 5-6 ppm "P" level is fine.

d) Insoluble: The content in the oil should be as low as possible and they will appear in the ester phase. The maximum value of 0.5% is to be respected to keep the ester product within the BD specification.

f) Saponification value and average molecular weight of oil: The SV is effectively used to determine the average molecular mass of oils and fats. Because of its large percentage of medium chain fatty acids, a lauric acid, will contain more ester bond than larger chain oil and hence have a higher SV; 240-250, for coconut oil compared to 190-195 for soybean oil. For bio-diesel production, this distinction is quite relevant in that the oils with high SV requires more methanol and produce more glycerol but less bio-diesel than larger chain fatty acid oils.

Hence it can be concluded that in case of a combined acid esterification /trans-esterification the following effects of various parameters, like, SV, AV, DG, MG and Average molecular weight of fatty acids etc, would emerge the scenario depicted in the following tables;

TABLE 1	FAME yield and methanol consumption based on SV, AV, EV and HV (combined TE and AE)					PFAD	UFO
	FOR 1000 Kg feed	rapeseed oil	Soybean oil	Palm oil	tallow		
	ARMM - FA	284	280	270	274	270	275
	FFA%	1.5	0.5	5	10	85	15
	AV	3	1	10.4	20.5	176.6	30.6
	SV	188.9	191.6	197.8	194.5	205.6	193.1
	HV	3	1	10.4	20.5	7.1	30.6
	EV	186	190.6	184.7	173.9	29	162.5
	FAME (kg)	1003.5	1004.2	1001.4	998.05	1040.9	994.8
	Methanol (kg)	107.9	109.4	112.9	111.1	117.4	110.3
	Glycerol (kg)	103.4	104.8	106.7	106.4	19.7	105.6
	water (kg)	1.0	0.3	3.3	6.6	56.7	9.8

Theoretical yield of Methanol, Water, Glycerol, FAME based on feed stock analysis (Combined TE and AE)

TABLE 2							
	FOR 1000 Kg feed	rapeseed oil	Soybean oil	Palm oil	tallow	PFAD	UFO
	ARMM - FA	284	280	270	274	270	275
	FFA%	1.5	0.5	5	10	85	15
	MG	0.5	0.1	2	4	2	7
	DG	2	0.8	6	12	5	16
	TG	96	98.6	87	74	8	62
	FAME (kg)	1003.3	1004.2	1000.4	996.1	1038.6	991.1
	Methanol (kg)	107.9	109.4	112.9	110.8	117.2	109.9
	Glycerol (kg)	103.6	104.9	109.1	108.1	21.8	108.9
	water (kg)	1.0	0.3	3.3	6.6	56.7	9.8

- The average relative molecular weight will have effect; but small, on the theoretical FAME (BD) yield.
- BD yield is affected more by the FFA content and the partial glyceride content of the feedstock. In case, the AV and HV are equal (or close) , *meaning that all partial glycerides and ffa in the raw material are originating from hydrolysis of TG*, Biodiesel yield and methanol consumption will be lower and glycerol/water production will be higher with increasing AV and HV.
- If the raw material contains more FFA than DG on a molar basis, as in case of PFAD, the AV will be much higher than the HV. This will result in a significantly higher FAME yield.

Catalyst:

The choice of the catalyst is one of the most important decisions to be made at the start of the biodiesel project. Three types are commonly used; KOH crystals, NaOH crystals (both to be dissolved in methanol) or Na-methylate.

- KOH:** is cheap, largely available product and solution in methanol will do the job as catalyst. However, to obtain the same conversion rate you need more catalyst compared to Na- based product and main problems are “K+” ions. K+ ions are found in glycerol phase, where they form a K-salt with the acid group used for acidification. The K-salt, have the disadvantage to have a very low solubility in glycerol, so immediately salts crystals are formed. A plugging risk of the equipment might be foreseen. These solids to be removed at glycerol treatment; a filter or a super decanter has to be installed. Has to have a very low pH value (pH level 1), which makes this job very difficult on the long term. The glycerol loss, lost with the salt, is another disadvantage.
- NaOH:** dissolving NaOH is an exothermic reaction so the vessel in which the operation is carried out, should be cooled in order to prevent excessive methanol loss through evaporation. So also, the formation of water will do the job difficult as the presence of water in the vicinity of process will be detrimental.
- Na-Methylate:** Although all the catalysts produce a high-quality biodiesel product, the sodium methylate catalyst provides the highest yield of biodiesel. Since feed-stocks costs of the vegetable oil or other tri-glyceride sources account for most of the variable cost of

biodiesel production (up to 85 percent), a higher yield of a few percent usually translates into substantial savings that more than compensate for the higher catalyst cost.

Sodium methylate has become the catalyst of choice for modern large scale bio-diesel production accounting for more than 70 percent of the bio-diesel produced in North America and it is successfully used in large scale production facilities for all major feed-stocks like virgin vegetable oils, animal fat and/or yellow grease.

Sodium methylate for bio-diesel production is typically supplied as solutions in methanol in concentration range of 25 percent to 30 percent, which have proven to be most advantageous. Safety and handling practices for sodium methylate solutions are very similar to safety and handling practices for methanol. Like methanol, sodium methylate solution is flammable and is handled safely by many people on a daily basis.

The major advantage of sodium methylate is the virtually water-free character of the catalyst solution. This results in higher yields, lower purification costs and more consistent bio-diesel quality. When mixing traditional hydroxides with methanol, hazardous solid handling is inevitable, and as a result, water is generated that will initiate unwanted side reactions.

Table 3 highlights the main benefits of using sodium methylate instead hydroxides. These advantages make it obvious why most producers rely on sodium methylate, especially since it has proven its favourable effects over the hydroxides, caustic soda/methanol, in many reference plants.

Table 4 highlights the effectiveness of sodium methylate, sodium hydroxide and potassium hydroxide in a reaction vegetable oil and methanol.

Table 3. Main benefits of using sodium methylate instead hydroxides

<i>Sodium methylate solution</i>	<i>Caustic soda/caustic potash</i>
Safety	Safety
No direct contact with product	Dangerous handling of caustic soda Exothermic reaction while mixing with methanol
<i>Economics</i>	<i>Economics</i>
Higher catalyst costs Liquid handling (lower labour costs) No mixing needed Better product quality Better bio-diesel yield	Lower catalyst costs Solid handling (higher labour costs) Higher water content (>10% in self-made catalyst solution) Higher purification costs Lower bio-diesel yield

Table 4. Effectiveness of sodium methylate, sodium hydroxide and potassium hydroxide in a reaction sunflower oil and methanol

	<i>Sodium hydroxide</i>	<i>Potassium hydroxide</i>	<i>Sodium methylate</i>
Bio-diesel Yield (wt%)	86,71 +/- 0,28	91,67 +/- 0,27	99,33 +/- 0,36

Performances of sodium methylate versus other catalysts (sodium hydroxide, potassium hydroxide) can be summarized as below:

- better reaction yield;
- lower soaps formation;

- lower chemicals consumption;
- glycerin of better quality;
- lower maximum allowable fatty acids content;
- better choice for medium/high capacities with vegetable oils;
- Less competitive for medium/low capacities and/or with animal fats and high acidity feedstock.

-Bio-diesel Production Process Options-

One of the major technology questions is whether to build a batch or a continuous flow bio-diesel plant. Batch reactors are generally not used in the production of large volume bio-diesel production since it is most efficient to operate the subsequent separation and purification steps in a continuous mode.

However some plants currently in operation are batch plants and produce discrete “runs” of product. These plants typically vent unused methanol into the air and do not recapture unused catalysts. This increases operating cost. Processing in discrete runs can at times create quality and uniformity differences in the final biodiesel product. As per the latest news from USA, it is apparent that motor engines are knocking down due to use of low grade of bio-diesel made from such ‘runs’

Due to the greater productivity, lower operating and labour costs, emissions controls and a more consistent product quality, best available technology is anyway; the continuous process.

It is possible to reuse excess methanol that has not become part of the biodiesel and it is possible to reuse the catalysts. Both are typically lost in the batch plants.

It is also evident that continuous flow plants are able to deliver larger quantities of higher quality and more consistent methyl ester product.

The major drawback to the continuous flow process appears to be the higher initial investment required. The continuous flow process generally requires a larger-scale plant, thus the initial capital outlay to build a continuous flow plant is generally higher.

Furthermore continuous process allows use of high-volume separation systems (centrifuges) which greatly increase throughput.

Table 5. Continuous versus batch reactor in biodiesel production

	Continuous	Batch
Yield	99,3	Max. 95%
Methanol recovery	YES *	NO
Heat recovery	YES	NO
Catalyst reuse	YES	NO

*After rectification both the methanol obtained at the top of the rectification column and the waste water obtained at the bottom of the column are fully recycled.

Reactors type:

Reactors can be placed into two broad categories, batch reactors and continuous reactors. Two of reactors within the continuous reactor category are continuous stirred tank reactors (**CSTRs**) and plug flow reactors (**PFRs**).

Continuous Process Systems:

A popular variation of the batch process is the use of continuous stirred tank reactors (CSTRs) in series.

The CSTRs can be varied in volume to allow for a longer residence time in first CSTR to achieve a greater extent of reaction. After the initial product glycerol is decanted, the reaction in second CSTR is rather rapid, with more than 98% completion not uncommon.

An essential element in the design of a CSTR is sufficient mixing input to ensure that the composition throughout the reactor is essentially constant. This has the effect of increasing the dispersion of the glycerol product in the ester phase. The result is that the time required for phase separation is extended.

There are several processes that use intense mixing, either from pumps or motionless mixers, to initiate the esterification reaction. Instead of allowing time for the reaction in an agitated tank, the reactor is tubular. The reaction mixture moves through this type of reactor in a continuous plug, with little mixing in the axial direction. This type of reactor, called a plug-flow reactor (PFR), behaves as if it were a series of small CSTRs chained together. The result is a continuous system that requires rather short residence times, as low as 6 to 10 minutes, for near completion of the reaction. The PFRs can be staged, to allow decanting of glycerol. Often this type of reactor is operated at an elevated temperature and pressure to increase reaction rate.

Ester treatment:

The ester phase leaving the decanter has too much glycerol and methanol. Glycerol is mostly removed by washing. Methanol is always removed by evaporation.

a) Ester washing: the basis of the operation is to remove glycerol, which is very hydrophilic product, by adding water to the ester. The washing water is charged with glycerol, methanol and some impurities. This mixture is very valuable as it contains a lot of glycerol, so it is added directly to the glycerol phase, just before the glycerin treatment. Thus limiting the water quantity limits the quantity of water to be evaporated in the glycerol. From there, the water can be recycled into a washing unit. This means that the bio diesel production unit can be kept effluent free.

b) Type of acid to be used for washing: Two main consideration here, glycerol quality and corrosion.

1. Glycerol quality: sulphates (both K and Na), are much less soluble in glycerol than chloride. This implies that the final concentration of the crude glycerin will be limited when using sulphates. Rarely more than 65-70% glycerin concentration is possible with sulphate, while in the case of chloride the concentration can be in the range of 85-88%. Less concentration means higher transportation cost for the same amount of pure glycerol and higher post-treatment cost. The sulphates are less soluble... thus special attention to the de-methanolization section of glycerol treatment.
2. Corrosion: chloride corrosion is really without a mercy; only after some weeks of operation leakage will start appearing if the choice of construction material is not proper.

Glycerine treatment:

The first step is acidification, of course, with a prior de-methanolization step. The main advantage being that we can avoid some acid resistant construction material. The aim of acidification is to split soap. The use of acid is discussed above, but in principle, if we use only one type of acid, then the salt formed in glycerol phase are homogeneous.

After acidification some fatty acid/fatty matter will float on the glycerol, which can be recovered, to be recycled in to the process, by simple decantation..

The glycerol fraction is neutralized to pH 7, and then the de-methanolization can start.

Glycerol specification:

- a) Concentration:** this is the main factor for price calculations. A generally acceptable concentration would range between 80-85%.
- b) Salt content:** in principle, salt must be as low as possible. The salt characteristics are of absolute importance.
- c) MONG:** (matter organic non glycerol) = non glycerol organic material, should be as low as possible, but in any case below 2%. In fact, we say about soap, ffa, and other impurities in the glycerol. MONG can be influenced by using right dose of catalyst and by doing good acidification at the glycerol treatment.

For example; from one of the operating plant elsewhere, crude glycerin having the analysis :Glycerol- 89%, Oil and Fatty Acid 1%, Salt -3%, moisture- 4-5 %, MONG - 4%. The oil is in the form of methyl esters and is not getting saponified with caustic. Hence at the time of distillation, the same is getting distilled of along with glycerin and gets contaminated with condensed glycerol. This subsequently spoils the bleaching bed of carbon, which is imported one and costly.

- d) Methanol:** should be less than 0.1%, which can be adjusted by using good stripping section and an appropriate temperature and vacuum condition.
- e) pH:** should be around 7-7.5. pH values above 9 gives a very viscous glycerol, which becomes very difficult to pump.

Methanol rectification:

This is the unit operation where maximum utility consumption is expected , mainly, steam as well as water in circulation and hence power consumption.

Generally the excess methanol for the Trans-esterification is ranging from 1.5 to 2 times of theoretical /stoichiometric amount. In case of acid esterification process, the excess can range between 3 to 10 times. In acid esterification process, lower the catalyst used, higher the excess is required.

Thus the steam and water consumption/circulation will be decided as the excess of methanol used as well as theoretical stages designed for rectification column.

The top pure methanol (99.9%) will be recycled and, at the bottom, pure water obtained. This water can be recycled for washing stage or released to the water effluent treatment plant.

Biodiesel commercial technologies:

A. – Starting from refined OIL

- Buy refined, de-gummed oil
- Trans - esterify
- Recycle any soaps
 - Convert to FFA with acid treatment
 - Save separately as co-product
 - Or save and convert to methyl esters in small batches
- Sell crude glycerin or upgrade or convert to other co-products

B. Starting from crude oil:

- FFA : < 2%
- PRETRET, caustic neutralization, silica treat
- Refined oil – Trans-esterify
 - Recover soap and with acid treatment recover fatty acids
 - Convert fatty acid to methyl esters by acid esterification
 - Small batch process
 - Neutralize remaining FFA in bio-diesel output and recycle.
- Glycerin is slightly better quality –
 - No soaps.

C. Starting from crude oil but with caustic strip during trans-esterification:

- FFA : < 4%
- De-gumming
- Caustic strip during trans-esterification
- Process Tri-glycerides with Trans-esterification
 - High soap level can cause foaming
 - Emulsifications
 - Reduces yields and creates problems
- Soaps comes out in glycerin
- Recover soap and convert FFA to Bio-diesel as in #2

D. Starting from HIGH FFA OIL;

- FFA : < 20 %
- React entire feedstock in Acid esterification
 - Convert FFA to bio-diesel
 - Remove water of reaction
 - Remove excess methanol and acids
- React entire esterified feedstock in trans-esterification
 - Use extra catalyst to neutralize acids, remaining fatty acids
- Recycle remaining soaps, FFA and re-introduce in to raw feed stock

E. Starting from PFAD or fatty acid distillate:

- FFA : > 90% (PFAD or fatty acid distillates)
- Use full acid esterification using Sulphuric acid catalyst
- Treat distilled fatty acids in two step Acid esterification
 - Convert FFA to bio-diesel
 - Remove water of reaction at every stage, No glycerin and soap
 - Remove excess methanol and acids,
 - Expensive equipment
 - Huge quantity of sulphuric acid to handle
 - Effluent handling and approval
- Fractional distillation to recover esters (bio-diesel)
 - Relatively Low Yields due to TG, DG, MG and un-sap in feed stock

F. Popular technology today for Indian bio-diesel Industry:

- FFA - 1 - 20%
- Pre-treat - de-gummed, silica/bleached, de-acidify
- Treat distilled fatty acids in two step Acid esterification
 - Convert Fatty acids to Methyl esters
 - Remove water of reaction at every stage
 - Remove excess methanol and acids
- Mix 20% pre-esterified ME with 80% refined feedstock- process entire 100% through trans-esterification
- Bio-diesel
- Recycle remaining soaps by converting Fatty acids and re-introduce in to acid esterification route
 - 100 % yield and no apparent process loss.

The product “Bio- diesel” itself:

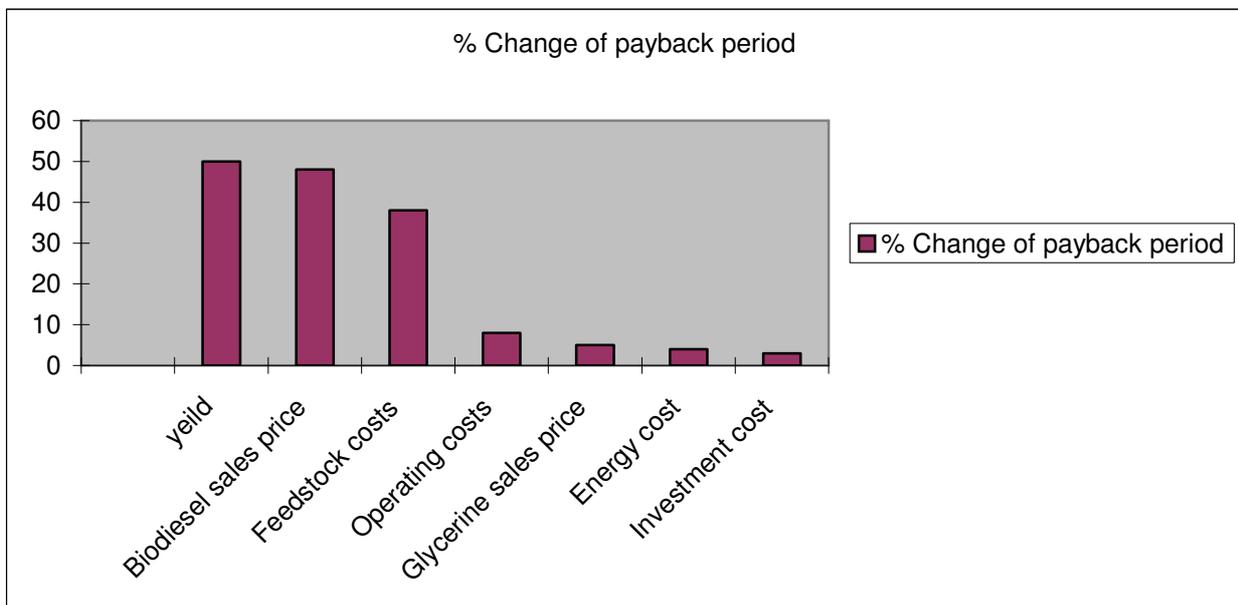
- Methanol content less than 0.1 % can be achieved.
- Water content allowed is 200 PPM max. The biodiesel is very hygroscopic. The water content in the storage tank will gradually go up at high speed e.g. more than 200 ppm/day, if the air has a high relative humidity. It is recommended that the nitrogen blanketing or to have tanks with floating roofs.
- Mono, di, and tri-glycerides – 0.8%, 0.2% and 0.2% respectively is the limit. The main reason to shoot up those values can be the incomplete reaction, which can be controlled by adjusting the doing of catalyst and proper reactor design.
- Free and total glycerol: 0.02% and 0.25% respectively. The free glycerol is never a problem if the washing is done effectively. A typical value obtained is 60 ppm at this stage.
- CFPP: (cold filter plugging point), there is lots of confusions about this property of biodiesel. This parameter was introduced for biodiesel, if and only if, to be used without mixing with petroleum diesel. The result is directly related to the type of feed stock used. The real correction is only possible by doing pour point depressors. **However, CEN decided that the CFPP requirement will not apply to the blended diesel fuel consisting 5% or less bio-diesel.**
- Oxidative stability: This term is often a delicate parameter, but nothing special about it to be discussed here.

Bio-diesel production – key factors and sensitivity analysis:

The key factors that decides the profitability of the projects are mainly,

- Yield
- Bio-diesel sales price
- Feedstock cost
- Conversion cost
- Glycerin sales price
- Energy cost
- Investment costs

The sensitivity analysis, as shown below, is based on as to how just 5% change in various key factors would change the economic profitability (static payback period) of bio-diesel production unit



Thus a change in yield by 5% e.g. 95% yields instead of 100% would result in the doubling the payback period time. The yield is mainly a matter of right choice of process technology. Once the technology is selected, the yield is defined and hence profitability of the project.

The same sensitivity is true for the sales price of bio-diesel. This price is determined by the local policies, fuel market etc. so that there is very little that investor can do about the situation.

The third major factor that is important is feedstock cost. Feedstock cost is the largest cost consideration in producing bio-diesel. The plant Capability to handle multiple feedstocks is ideal to maintain control of total costs. Soybean or Rapeseed oil is expensive feedstocks but have minimum conversion costs. More difficult feedstock is less expensive but have higher conversion costs.

All other factors such as auxiliaries, utilities, and investment costs are important, but even when putting then together, they do not show the same effect as only one of the three key factors considered above.

PLANNING, SITE SELECTION AND CRITICAL PARAMETERS. -Guidelines for investors

- Feedstock Sourcing:

Do you have control of your own feedstock supply (seeds – crude or refined vegetable oil)?
If you are dependent on an external supply, how many potential suppliers are within a 300 km radius?

Can you sign a long-term contract with one of these suppliers to insure adequate feedstock?
Will the feedstock suppliers in the area deliver by truck or rail, and at what frequency?

- Glycerine Outlet:

Where are the closest potential buyers of glycerine?
What quality of crude glycerine (H₂O, MeOH, soap, FFA, salt, MONG, etc) will they purchase, and at what price relative to Pharma grade refined glycerine?
Will the glycerine refiners in the area want delivery by truck or rail, and at what frequency?
Do you need to install your own glycerine refinery?

- Process Plant Size:

What plant size will meet the short and long term needs of the local bio diesel market?
How does local feedstock availability limit plant size?
What minimum plant size is required to provide a competitive conversion cost in the long-term?

- Transportation Proximity

Is the site adjacent to an active freight rail system?
Does the site, or can the site, have a rail siding installed with sufficient length of track?
At what frequency are rail switches possible, and how will the rail cars be moved for loading/unloading?
Is the site in close proximity to a highway?

- Specific Parcel of Land:

Does the site have sufficient space for the process plant (with surrounding safe area), tank farm, utility building, office building, rail siding and truck route?
Does the site have sufficient extra space for a future bio-diesel plant expansion or glycerine refinery?

- Shared Infrastructure:

Does the site already have a process plant staff (management, marketing, purchasing, maintenance and quality control) that can be shared to offset conversion costs?
Does the site have already feedstock tanks to reduce feedstock (freight) costs?
Does the site already have utilities that can be shared?

- Safety:

Biodiesel plants use a considerable quantity of highly flammable liquid (methanol & sodium methoxide) and hence a safety aspect becomes an important criterion.

The process plant must be designed as a hazardous area environment with the hazardous areas within/and adjacent to the process building.

The methanol and sodium methoxide storage tanks must be designed in accordance with.

Plant needs to respect the required regulation and be fully explosion proof according to local regulations.

Working with a professional technology supplier and construction company that both understand building plants/equipment for hazardous area classifications is critical to personnel safety and plant profitability

- Quality:

All biodiesel leaving the facility must meet EN specs (ASTM for US) at the minimum. Biodiesel leaving the facility should also meet moisture, pour point, cold filter plug point specs, if required.

Purchasing a well-designed plant with adequate automation, and properly managing storage and transportation logistics, are both critical factors to maximizing uptime and profitability.

Biodiesel should be continuously pumped from the process to a shift-tank or day tank and analysed before being sent to storage.

It is critical that a bio-diesel plant have a fully equipped lab with a qualified chemist that understands the chemistry and unit processes in the plant well enough to trouble-shoot feedstock & process issues and give the operations staff the assistance they need to maintain acceptable quality on an ongoing basis.

- Operating Costs:

Approximately 85% of operating cost of a bio-diesel plant is the cost to acquire the feedstock.

Securing your own feedstock to insure supply at a fair price, and minimizing the freight to deliver the feedstock to the biodiesel plant, is both critical factors in controlling profitability.

An alternative to controlling supply is to have a flexible process to handle multiple feedstock sources (such as crude oil, palm oil, high ffa feedstock, animal fats and UFO).

Chemical consumptions, utility consumptions and maintenance costs (50-75% of the conversion cost) are more a function of the technology than plant size.

Selecting automated, continuous process technology is a critical factor in controlling plant profitability

Manpower, taxes, insurance and depreciation (25-50% of conversion cost) are more a function of plant size than technology.

Selecting a plant large enough to take advantage of economy of scale (capital & manpower) is a critical factor in controlling plant profitability.

- Capital Costs:

Process equipment only accounts for 25-35% of total capital cost in a typical biodiesel plant. Choosing a competitive, qualified contractor for constructing the overall facility is a critical parameter in controlling total capital cost.

Approximately 65% of the capital cost of a bio-diesel plant is in the process building, and 35% of the capital cost is in the supporting infrastructure.

Locating a plant on a site that already has as much supporting infrastructure as possible is a critical factor in minimizing capital cost.

Finally, and last but not the least, it is fundamental to choose a reliable supplier to guarantee a fast project execution and plant start-up to take profit of current favourable conditions

The above guidelines are applicable for both, small capacity and large capacity bio-diesel manufacturing plants.