Production of Biodiesel from Used Kitchen Oil Using Hydrodynamic Cavitation

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Abstract:- *In 21st century it is need of the hour to reduce consumption of fossil fuel, since their stock is limited and may lead to complete depletion in near future. Biodiesel is the best alternative fuel source. The easiest way of obtaining biodiesel is by trans-esterification of triglycerides or fatty acids with alcohol in the presence of a strong catalyst (base, acid or enzymatic). Cavitation is formation, growth and subsequent collapse of micro bubbles or cavities occurring in extremely small interval of time (milliseconds) and at various lactations in the reactor, releasing tremendous amount of energy. The sudden collapse of cavities under pressure enhance the mass transfer between oil, methanol and catalyst. Hydrodynamic cavitation forms charge particles in oil and alcohol mixture, transesterification gives fatty acids of methyl ester/ ethyl ester. This article reviews not only cheap feed stock but also production method for biodiesel.*

Keywords:-**Biodiesel, Transesterification, Waste Kitchen Oil (WKO), Cavitation, FAME, Free Fatty Acids, etc.**

1. Introduction:-

Biodiesel has a huge potential as a fuel as well as has capacity to decrease the rate of emission of air pollutants such as particulate matter, carbon monoxide, carbon dioxide, sulphur derivatives of gases and trace nitrogen, other minor gases (R. ANR et al, 2016). Hence, we have selected area of research of renewable energy source as "Biodiesel". It is not commercialized because of more prices of the feed stock and production economy (A.R. Gupta et al, 2015). Cost of vegetable oil plays precious role in biodiesel production. As we observe the market prices of oil has much more but variety of oils may be able to use for production. But this path is not achieving more economy (Nitin S. Kolhe, 2017). The studies done by Mittelbach and En-zelsberger on frying oil suggest that, during frying, primarily thermolytic, oxidative, and hydrolytic reactions occur. Due to these reactions along with methyl esters, dimeric fatty acid methyl esters are also formed (Mittelbach et al, 1999). Due to lack of availability it is not preferred. India produces almost 9.2 million tons of waste cooking oil per year, which is highest in all nations (thebetter India web, 2017). The easiest method for producing biodiesel is the transesterification of triglycerides or fatty acids with an alcohol in the presence of a strong catalyst (acid, base, or enzymatic). These Free Fatty Acids (FFAs) may be taken from used kitchen oil. This waste kitchen oil are ground nuts, soya bean, mohori, palm, etc. These have been easily tranesterified. The alkali-catalyzed reaction gives a better conversion in a less time with small amounts of FFA.

Transesterification is more favorable. Industrial processes mainly favor base catalysts because alkaline catalysts are less corrosive than acidic compounds, hence we have used alkaline (Singh *et al.,* 2007). Alcohol and oil are miscible together, so transesterification reactions have limitation in terms of mass transfer and hence require mixing (Ji*et al*., 2006). So, to overcome this drawback we opted hydrodynamic cavitation. The worldwide market for essential biodiesel growth rapidly and nowadays a lot of scientific research presently focused on the industrial development together with environmental preservation by used different techniques of biodiesel production as Acoustic Cavitation, Hydrodynamic Cavitation, Combine Hydrodynamic and Acoustic Cavitation, Power Ultrasound.

2. Origin of the problem:-

All over the world million tons of waste kitchen oil is generated in hotels, houses, functions, but not reused in many countries. It increases the water pollution if dumped in a sanitary as well as require a special tertiary treatment in treatment plants. Oil is the most commonly utilized in the world due to its pleasant taste in food and nutritional values. Because of the huge consumption of oil tremendous amount of liquid waste is produced. This waste mainly includes soyabeen oil, coconut oil, ground nut oil, palm oil, mohori oil. These oils contain free fatty acids which are not suitable for reuse in kitchen and its quality, taste, order, freshness ultimately decrease.

Fig.1 Food Industry Kitchen Waste oil

Fig.2 Food Store and House Waste Oil

Therefore, instead of throwing out waste oil, it can be utilized for biodiesel production. The composition of biodiesel generated depends on the type feed oil used and method of production. The quality of biodiesel produced directly depend on well optimized method of production and refining of biodiesel. The cooking process of kitchen causes the vegetable oil, Triglyceride to breakdown to form, Monoglycerides, Diglycerides, and free fatty acids (FFAs) (Kathleen F et al, 2014). Not only the amount of heat but also water in the frying increases the hydrolysis of triglycerides, therefore it causes a growth of the Free Fatty Acids (FFAs) in the waste cooking oil. In a study on the fatty acid (Nabanita Banerjee et al, 2014), It had been concluded that the vegetable oil contains acids like Myristic(Tetradecanoic), Palmitic(Hexadec-anoic), Stearic (n-Octadecanoic), Oleic , Linolenic, Arachidic and other fatty acids. Among these oleic as well as linoleic had detected to be in more amounts. The preferred used vegetable oils for kitchen purposes are generally olive, sunflower and peanut ones. Other study (A Sunthitikawinsakul et al, 2012) concluded that to obtain a good yield of product (above 90%), the concentrations of palmitic, oleic and linoleic acids should be about 37, 50 and 12% v/v and more. In favors of concentrations of triglyceride, diglyceride and monoglyceride, investigation shows that waste kitchen oil with FFA (wt/wt %) 8.42 and Acid value (mg KOH g^{-1}) 16.6, had Triglyceride concentration (%) of 84, Diglyceride concentration (%) of 7.0 Monoglyceride concentration (%) of 0.3 (Kathleen F et al, 2014).

3. Essential Biodiesel:-

Biodiesel is a petroleum based fuel obtained from animal fats, vegetable oils and used waste cooking oil includes triglycerides. Trans-esterification is the most familiar method and leads to mono-alkyl esters of vegetable oils and fats, called bio-diesel when used for fuel purposes of any convention. Biodiesel is become more attractive presently because of its eco-friendly benefits and also it is made from renewable resources. Bio-fuels can be produced across the world using resources that are available locally, due to control foreign exchange for buying crude oil as well as increases the country's economy (Cherukuwada .V et al, 2014). Generally biodiesel has better burning than diesel. India is importing fossil fuel from Arab countries, so most of our economy transfers into that countries and simultaneously our currency has low value in world market. Hence, we want to develop this type of fuels to develop the nation. However World Energy Forum (WEF) shows that the fossil fuel will be come to its peak production in next 10 decades (Lim and Lee, 2012). Vegetable oils can be used as a replicable for petroleum diesel by blending them directly with fuel or by enhancing their properties through a number of available technologies (Ng et al., 2012).

4. Chemical constituents of Essential Biodiesel:-

Biodiesel is a mixture of alkyl ester (AE) and has good calorific value. Basic component for preparation of these ester mixture is glycerin. Alkyl groups may be Ethane, Methane, and Propane. Methane derivatives of ester have better performance in the performance of biodiesel. So, researches develop a process which gives methane derivatives. Triglycerides are first converted step wise to diglycerides, then monoglycerides and finally glycerol liberating a mole of ester in each step (Han H. et al, 2005). In this biodiesel production a high quality of biodiesel is recovered as a bi-product (Cherukuwada .V et al, 2014). Biodiesel has low melting point as compared to vegetable oil, hence a problem of solidifying of blend vegetable oil is solved. We can blend biodiesel with diesel.

5. Waste kitchen oil as feedstock of biodiesel:-

The term "waste kitchen oil" (WKO) refers to vegetable oil which has been used in food production and which is no longer viable for its intended use. WKO arises from many different sources, including domestic, commercial and industrial. WKO is a potentially problematic waste stream which requires to be properly managed. The disposal of WKO can be problematic when disposed, incorrectly, down kitchen sinks, where it can quickly cause blockages of sewer pipes when the oil solidifies. Properties of degraded used frying oil after it gets into sewage system are conducive to corrosion of metal and concrete elements. It also affects installations in waste water treatment plants. Thus, it adds to the cost of treating effluent or pollutes waterways (Szmigielski, Maniak & Piekarski, 2008). Any fatty acid source may be used to prepare biodiesel. Thus, any animal or plant lipid should be a ready substrate for the production of biodiesel. The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials - the food versus fuel dispute (Pimentel *et al.,* 2009; Srinivasan, 2009). There are concerns that biodiesel feedstock may compete with food supply in the long-term. From an economic point of view; the production of biodiesel is very feedstock sensitive. Many previous reports estimated the cost of biodiesel production based on assumptions, made by their authors, regarding production volume, feedstock and chemical technology. In all these reports, feedstock cost comprises a very substantial portion of overall biodiesel cost (Haas *et al.,*2006) developed a computer model to estimate the capital and operating costs of a moderately-sized industrial biodiesel production facility. Calculated production costs included the cost of the feedstock and of its conversion to biodiesel. The model is flexible which can be modified to calculate the effects on capital and production costs of changes in feedstock cost, changes in the type of feedstock employed, changes in the value of the glycerol co-product and changes in process chemistry and technology. The authors reported that for biodiesel produced from soybean oil, the cost of the oil feedstock accounted for 88 % of total estimated production costs (Haas *et al.,* 2006). Marchetti, Miguel & Errazu, (2008) used a conceptual design of alternative production plants with a techno-economic analysis in order to compare these alternatives. In all cases, more than 80 % of the production cost is associated with the feedstock itself and consequently, efforts should be focused on developing technologies capable of using lower-cost feedstock, such as recycled cooking oils. Reusing of these waste greases not only reduce the burden of the government in disposing the waste, maintaining public sewers and treating the oily wastewater, but also lower the production cost of biodiesel significantly. (Refaat, 2010)

6. The biodiesel production processes:-

Biodiesel is having a specified mechanism for production processes these are given as below. These are esterification, trans-esterification, supercritical method, bubble-column reactor method, microwave method, hydrodynamic cavitation.

6.1Esterification process:-

Esterification, as it applies to biodiesel production, is the chemical reaction by which a fatty acid, typically a free fatty acid in degraded or second-use oil, reacts with an alcohol to produce an alkyl ester and water. The process differs from the transesterification reaction in that the reaction occurrs directly between the alcohol and the fatty acid molecule. The intermediate steps of cleaving the fatty acid chains from the glycerin backbone is not present. For this reason, no glycerin is produced during the esterification reaction. The following formula shows the basic esterification reaction with methanol. A fatty acid molecule reacts with a methanol molecule to form a methyl ester plus a water molecule:

$$R1\ COOH \quad + \quad CH_3OH \quad \leftrightarrow \quad R1\ COO\ CH_3 + \quad H_2O$$

Free fatty acid Methanol Methyl ester Water

The above formula was adopted from Deshmane, Gogate & Pandit, (2009) and represents the basic chemical reaction for all industrial esterification reactions using methanol as the alcohol

Conventionally, virgin vegetable oils and high-grade animal fats are the feedstock of choice for biodiesel production due to low levels of impurities, such as free fatty acids and sulfated proteins, which can cause problems with processing and final product quality. Rapeseed alone comprises of roughly 84% of the lipid stocks used for biodiesel production. By comparison, sunflower and palm oil each represent 13% of the feed stocks with soybean trailing with a 1% share. All of other feedstock such as waste cooking oils, animal fats, jatropha, peanut, mustard, etc. make up the remaining 2% (Pahl, 2005).

6.2 Transesterification process:-

The chemical reaction by which a lower alcohol reacts with a triglyceride to yield a fatty acid alkyl ester is known as transesterification. It occurs easily with the lower alcohols such as methanol or ethanol. The process is slow under normal conditions without the presence of a catalyst. Traditionally, an alkaline catalyst such as sodium or potassium hydroxide is used to catalyze and accelerate the reaction at standard temperatures and pressures. The catalytic reaction is complicated; however the necessity for a catalyst arises from the relative insolubility of alcohol in oils. Catalysts provide a phase-transfer as well as an ion exchange effect which reduces reaction times by many orders of magnitude (Mittelbach & Remschmidt, 2004).

Transesterification consists of a number of consecutive, reversible reactions (Schwab, Bagby & Freedman, 1987; Freedman *et al.,* 1986). The triglyceride is converted stepwise to diglyceride, monoglyceride and glycerol. A mole of ester is liberated at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol.

Triglyceride (TG) + R'OH↔ Diglyceride (DG) +R'COOR1

Diglyceride (DG) + R'OH ↔Monoglyceride (MG) + R'COOR2

Monoglyceride (MG) + R'OH↔ Glycerol (GL) + R'COOR3

The reaction mechanism for alkali-catalyzed transesterication was formulated as three steps (Eckey, 1956). The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. The catalyst such as NaOH, KOH,K_2CO_3 or other similar catalysts were mixed with alcohol and alkoxide group is formed (Sridharan & Mathai, 1974). A small amount of water, generated in the reaction, may cause soap 21 formations during transesterification.

The catalyst used for these reactions as follows:

A) Alkali catalyst: These type use methoxide, ethoxide as well as any type of oils, frying, crude, refined. The main alkali catalyst are sodium hydroxide, potassium hydroxide.

B) Acid Catalyst: Acid catalyzed transesterification is most convenient type to make biodiesel if the feed have high free fatty acid continent.

C) Enzyme Catalyst: Enzyme catalyzed procedure, using Lipase as a catalyst, but are very much expensive for industrial scale. Also have three step process to achieve 95% conversion.

7. Essential Biodiesel Production Methods:-

Essential biodiesel is used in a wide variety of consumer goods such as fuel for vehicles; operating engine rooms in biogas plant and produce energy. The world production and consumption of essential biodiesel are increasing very fast. Production technology is an essential element to improve the overall yield and quality of essential biodiesel. Essential biodiesel is obtained from waste vegetable oil by Hydrodynamic Cavitation.

7.1 Hydrodynamic Cavitation Method:-

Cavitation is the formation, growth and subsequent collapse of micro bubbles or cavities occurring in extremely small interval of time (milliseconds) and at multiple lactations in the reactor releasing large magnitudes of energy. The various effects of cavity collapse are creation of hot spots, releasing highly reactive free radicals, cleaning of solid surfaces and enhancement in mass transfer rates. The collapse of bubbles generates ‘‘hot spots’’ with transient temperature of about 10,000 K, pressures of about 2000atm .Cavitation is classified into four types based on the mode of generation viz. Acoustic, Hydrodynamic, Optic and Particle, One of the alternative techniques for the generation of hydrodynamic cavitation is by use of hydraulic devices where cavitation is generated by the passage of the liquid through a constriction such as valve, orifice plate, venturi etc. of these treatment, but these offer higher energy efficiencies, more flexibility and higher potential for scale-up as compared to their acoustic counter parts. In hydrodynamic cavitation (HC) the intensity of the cavity collapses (final collapse pressure) due to reduction in cavitation number and hence the cavitational yield is very much dependent on the surrounding pressure field (turbulent pressure field). The intensity of turbulence depends on the magnitude of the pressure drop and the rate of pressure recovery, which in turn depends on the geometry of the constriction and the flow conditions of the liquid, i.e., the scale of turbulence. The intensity of turbulence has a profound effect on cavitation intensity. Thus, by controlling the geometric and operating conditions of the reactor, the required intensity of the cavitation for the desired physical or chemical change can be generated with maximum energy efficiency.

Hydrodynamic cavitation (HC) can be generated by the passage of the liquid through a constriction such as an orifice plate. When the liquid passes through the orifice, kinetic energy/velocity of the liquid increases at the expense of the pressure. If the throttling is sufficient to cause the pressure around the point of vena contracta to fall below the threshold pressure for cavitation (usually vapor pressure of the medium at the operating temperature), millions of cavities are generated. Subsequently as the liquid jet expands, the pressure recovers and this results in the collapse of the cavities. During the passage of the liquid through the constriction, boundary layer separation occurs and a substantial amount of energy is lost in the form of a permanent pressure drop. Very high intensity turbulence occurs on the downstream side of the constriction; its intensity depends on the magnitude of the pressure drop, which, in turn, depends on the geometry of the constriction and the flow conditions of the liquid. The intensity of turbulence has a profound effect on the cavitation intensity. Thus, by controlling the geometric and operating conditions of the reactor, one can produce the required intensity of the cavitation so as to bring about the desired change with maximum efficiency. Also the collapse temperatures and pressures generated during the cavitation phenomena are a strong function of the operating and geometric parameters.

Below figure shows a typical setup to generate cavities hydrodynamically. The pressure-velocity relationship of the flowing fluid as explained by Bernoulli's equation can be exploited to achieve this effect. The flowing liquid, when it passes through a mechanical constriction, say an orifice or a partially throttled valve, venture or an orifice (part a in Figure 11), its velocity increases accompanied by increase in kinetic energy and corresponding decrease in the local pressure (part b in Figure 11. If the throttling is sufficient to reduce the absolute local pressure below the vapor pressure (at the operating temperature), spontaneous vaporization of the medium in the form of micro-bubbles (nucleation) occurs.

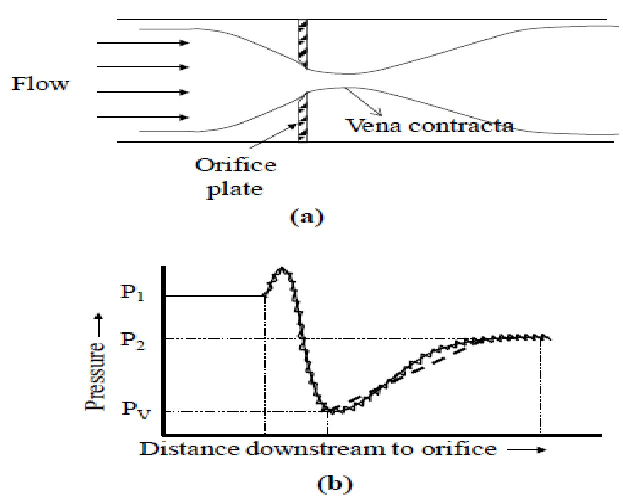

Fig 3: Fluid flow & Pressure variation in hydrodynamic cavitation set-up

A dimensionless number known as cavitation number is used to relate the flow conditions with the cavitation intensity. Cavitation number is given by the following equation:

$$C_v = \left(\frac{P_2 - P_v}{\frac{1}{2}\rho v_o^2} \right)$$

Where, P_2 is the fully recovered downstream pressure, P_v is the vapor pressure of the liquid, V_o is the velocity at the throat of the cavitation constriction.

In hydrodynamic cavitation all parameters depends on the geometry of cavitational device and the operating pressure. The important parameters which decide the efficiency and the overall cavitational yield are:

- Inlet pressure and the cavitation number
- Physicochemical properties of liquid and initial radius of the nuclei;
- Size and shape of the throat and divergent section (in the case of venturi)
- Percentage free area offered for the flow

The effect of the various design and operating parameters mentioned above has been studied extensively in terms of the collapse pressures on the basis of the numerical simulations using bubble dynamics equations and also on the basis of experiments done in different reactors.

The results of the numerical simulation in hydrodynamic cavitation were carried out also consistent with the experimental observations. The experiments have carried out optimization of the important geometrical parameters of a cavitating venturi. They have found that the ratio of the perimeter of the venturi to the cross sectional area of its constriction quantifies the possible location of the inception of the cavity. The ratio of the throat length to its height (in the case of a slit venturi) controls the maximum size of the cavity and the angle of the divergence section controls the rate of collapse of a cavity. Based on the numerical study, it was concluded that a slit venturi ($\alpha = 2.7$) with the slit length equal to its height (1:1) and a half angle of divergence section of 5.5 degrees is an optimum geometry for best cavitational activity.

All of the above studies depicted that, in hydrodynamic cavitation, the cavitational yield (efficiency of hydrodynamic cavitation in bringing about the desired changes physical and chemical changes) depends on the geometrical parameters as well as on operating parameters (operating pressure and cavitation number).

7.2 Hydrodynamic Cavitation System:-

The hydrodynamic cavitation system was fed with 6420 g of used frying oil. Potassium hydroxide prefers as catalyst on wt % basis of oil was mixed with known quantity of methanol added to the reactor (Nitin S.et al, 2017). The methanol quantity had been taken as per the different molar ratio of alcohol to oil (i.e. 1410 g for 6:1 molar ratio, 1060 g for 4.5:1 molar ratio and 705 g for 3:1 molar ratio). An extra amount of methanol was used to take care of the reversible reaction. To optimize the catalyst concentration, the reactions were carried out separately using two different KOH concentrations i.e., 0.65 and 0.985% KOH with optimized quantity of methanol (Khan M.A., 2010). The reaction mixture was circulated through the cavitation zone for longer time i.e. 1 h. The temperature achieved by cavitation and circulation effect was around 45 °C. In order to quench the reaction each sample was taken in a vial containing 31% H_2SO_4 solution in water. Reducer and gate valve are alternatives instead of orifice plate and venturimeter. Gate Valve and reducer were connected in series Favorable Cavitation occurred at 125 psi static pressure in reduced section and flow was 16.95 liter per min. Controlling this parameter, transestérication reaction yielded Fatty Acids of Methyl Ester (biodiesel) and glycerin. By separating these layers we get biodiesel which has great significance.

8. Literature Survey:-

Sr. No	Raw Material	Catalyst	Molar ratio (Methanol :oil)	Conversion	Author
1	Used Frying Oil	KOH	4.5:1	93.6%	Nitin S. Kolhe, 2017.
This paper gives intro of biodiesel production using hydrodynamic cavitation as well as separation and purification study of methyl esters yielded encouraging results.					
2	Crude Palm Oil And Rubber Seed Oil	KOH	8:1	90%	Suzana et al., 2015
The study of esterification and transesterification in hydrodynamic reactor had been done.					
3	Waste Cocking Oil	KOH/NaOH	6:1	94.3	Mohammed et al., 2015

There are various method in laboratory scale such as bubble column, pilot plant, batch reactor and each having different speciality such as catalyst amount, temperature.					
4	Commercial soyabeen Oil	NaOH	9:1	100%	Francisco et al., 2009
This paper evaluates and optimizes the production of biodiesel from soybean oil and methanol using sodium hydroxide as catalyst.					
5	Waste Cooking Oil	NaOH	6:1	96.54%	Altic et al.,2010
Various catalyst has been analysed in thesis and got the overview for the best. There was a research of new method for production of biodiesel.					
6	Cooking Oil	KOH	6:1,4.5:1	>90%	Amit pal et at., 2013
The presented research uses mechanical stirring method for transesterification reaction for production of biodiesel.					
7	Soyabeen Oil	NaOH	(ethanol)10:2	91.8%	S. Rodrigues et al., 2009
The process variables alcohol to oil ratio and catalyst to oil ratio were statistically significant regarding the yield of ethyl esters. The optimal operating condition had obtained applying an alcohol to oil molar ratio of 10.2 and a catalyst to oil weight ratio of 0.0035.					

Conclusion:-

From this review we conclude that biodiesel is environmental friendly and renewable fuels compare to diesel fuel. It is conclude that catalyst potassium hydroxide as well as solvent methanol yields better conversion of waste kitchen oil to FAME. The hydrodynamic cavitation is novel technique to minimize the cost of production of biodiesel. Biodiesel derived from renewable domestic resources, thus reducing dependability on and preserving petroleum. It is domestically produced, have offered the possibility of reducing petroleum consumption. Reductions of most pollutant emissions as compared to conventional diesel fuel, generating lower emissions of hydrocarbons not only particulates but also carbon monoxide. Biodiesel has a higher flash point greater than 150 °C, indicating that it offers a very low fire hazard; leading to safer handling, transport as well as storage. Engine wear is reduced due to greater lubricity than diesel. In fact, biodiesel can be used as a lubricity enhancer for low-sulphur petroleum diesel formulations. Toxicity tests shown by biodiesel are considerably less toxic than diesel. So, biodiesel surly used direct in most diesel engines without requiring any engine modifications.

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