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Review on Production of Biodiesel Through Hydrodynamic and Acoustic Cavitation

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ABSTRACT:

With the decreasing fossil fuel resource and the hike in prices for petroleum based diesel, biodiesel is an exceptional alternative as it is renewable and having better combustion performance. Therefor synthesis of biodiesel must be an important objective that should be taken into consideration. The conventional process involves mechanical stirring which has high reaction time and limited yield. Cavitation helps in mitigating this by increased turbulence which overcomes the resistances of mass transfer and promotes higher yield and shorter reaction time. Intensification of biodiesel conducted by hydrodynamic cavitation and acoustic cavitation is a potential method in which mass transfer limitations can be terminated. The present review aims at understanding the hydrodynamic cavitation and acoustic cavitation, the methods of generation of cavitation advantages of the hydrodynamic cavitation over acoustic cavitation and the operating effects of hydrodynamic and acoustic cavitation with various parameters into considerations such as mole ratio, output power, geometry of the constrictions, inlet pressure, type of cavitating device etc. The Biodiesel yield obtained also depends on factors like reactions, raw material, types of catalyst and excess of alcohol. A comparative study between the hydrodynamic and acoustic cavitation with respect to energy efficiency and yield is viewed for learning the further advancements that can be made.

KEYWORDS: Capitation, Process Intensification, Hydrodynamic Cavitation, Biodiesel, Acoustic capitation.

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INTRODUCTION:

Conventional fuels cause air pollution by emission of sulfur dioxides, carbon dioxides, particulate matter and other gases. Present era is facing tremendous problems pertaining to energy sustainability, pollution of environment and rising fuel price.Due to rapid population and industrialization, growth on global scale, demand of crude oil is increasing which is leading to spike in price of petroleum.Energy demand projection stipulate to develop new renewable energies to ensure energy security worldwide[1] .Biodiesel is a renewable, biodegradable and non-toxic alternative to fossil fuel. Due to varied advantages including low cost and greenhouse gas reduction potential, it is nowadays used all over the world especially in developed countries like USA, France, and Brazil. It can be used in conventional form or also can be blended with petroleum diesel that can be used in compression ignition engines. Biodiesel manufacturers are focusing their attention to use low-cost feedstock such as waste cooking oil to ensure economic viability in biodiesel production.

Biodiesel production aims to attain good yield by selecting suitable and cheap feedstock such as virgin vegetable oils, non-edible oils ,used cook oils and animals fats. Feed used for biodiesel production must have low fatty acid content. The edible vegetable oil which can be used as raw oil for biodiesel production include soybean oil, sunflower, palm oil, canola and peanut oil and non-edible oils such as sea mango, jatropha, rubber seed and pongamiapinnata. Waste cooking oil(WCO) is cheaper than refined vegetable oils and therefore has become a promising alternative feedstock to produce biodiesel. Waste cooking oil released into the environment without proper treatment causes environmental pollution. So in order to prevent pollution and also to reduce the total cost of production, waste cooking oil is best raw material[2] Development of an efficient catalyst is essential to have a better yield and an environmentally sound synthesis.There are three categories of catalysts used for biodiesel production which are alkalis, acids and enzymes As compare to enzyme catalysts, alkali and acid catalysts are more commonly used in biodiesel production.However, enzyme catalysts have become more attractive recently as it can avoid soap formation and the purification process is simple to accomplish. [3]

Biodiesel can be synthesized by esterification,transesterification and inter-esterification.Oil feedstocks containing more than 4% free fatty acids such as animal fats and recycled greases go through an acid esterification process to increase the yield of biodiesel. The transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol.Due to the reversibility of the reaction, an excess of alcohol is required to shift the equilibrium towards products formation. Furthermore, glycerol formed during the process is immiscible with the fatty acid methyl esters, therefore, leaves the reaction mixture and favors the completion of the reaction.An interesterification reaction with methyl acetate results in triglycerides getting converted into methyl esters and triacetin. Esterification can form biodiesel but is only applicable if there is higher amount of free fatty acid present so that it is easily converted to esters. Transesterification is the most common reaction carried for the synthesis but it forms low purity glycerol reducing the economy of the process. In the case of Inter-esterification, triacetin is formed as a byproduct which is a high valued product that is used as plasticizer and gelatinizing agent. Hence comparatively it is more economically feasible.The conventional approach for the synthesis has moderate efficiency with high reaction time which isn't a suitable approach. It is due to the mass transfer limitation since acid and alcohol forms immiscible phase in the system.Cavitation is an alternative approach which can eliminate this limitation and improve the yield. The present review provides a detail analysis on different aspects pertaining to Acoustic and Hydrodynamic cavitation and their effects on the biodiesel yield.

CAVITATION:

Cavitation is the activity of cavities or bubbles in liquid. It is formed when a liquid is subjected to rapid changes in pressure resulting in the formation of cavities at low pressure. When subjected to elevated pressure conditions, the voids implode and can generate an intense shock wave which releases large magnitudes of energy over a very small location resulting in very high energy densities. Cavitation phenomena consist of three steps: (a) nucleation (b) growth of cavity and (c) adiabatic collapse. These three steps are affected by the different geometric parameters [4]In cavitation, two aspects are of huge significance, the maximum size attained by the bubble before an explosive collapse and the life of the bubble. The maximum size reached by the bubble determines the degree of the pressure pulse and hence the cavitation intensity that can be obtained in the system. The life of the bubble determines the distance traveled by the bubble from the point where it is generated before collapse.[5] The Cavitation number (Ca) is a dimensionless number used in flow calculations that measures the resistance to the flow. Higher the cavitation numbers, sleek are the chances for cavitation to occur whereas lower it is there are more probabilities for cavitation to occur.In like fashion, if cavitation is occurring then lowering the cavitation number by reducing the static pressure or by raising the flow speed will increase the extent of cavitation and increasing it may eliminate cavitation completely. The two principal types of cavitation are Hydrodynamic cavitation whichis produced by pressure variation in a flowing liquid causedby the velocity variation in the system and Acoustic cavitationis a result of pressure variation in a liquid when ultrasound wavespass through it. Here the pressure variations in the liquid are affected using sound waves, usually ultrasound.

In hydrodynamic cavitation,the intensity of collapse of the individual cavities with respect to temperature and pressure is low.The number of cavitation events and their intensity to certain extent can be effectively controlled by adjusting the geometrical and operating parameters.The interior of the cavity are mainly at extreme conditions of temperature and pressure due to the adiabatic nature of the cavitational collapse. The contents of the cavity undergo breakage of bonds to generate free radicals. In the cavity- liquid interfacial region, the temperature is high enough to induce reactions via free radical mechanism. The free radicals formed in the cavity and interface region travel to the bulk liquid and undergo reaction. The major physical effects include generation of shock waves,Liquid microjet formation and Interfacial turbulence.This helps increasing the mass and heat transfer rates.[6]

Ultrasonic irradiation causes cavitation of bubbles near the interface of the alcohol and oil phases. As a result, minute bubbles are formed. The random collapse of the cavitation bubbles disrupts the interface and impinging of the liquids creates micro jets, leading to mixing of the system near the interface. The cavitation may also lead to a localized increase in temperature at the interface enhancing the transesterification reaction. Because of the formation of micro jets and localized heat formation neither agitation nor heating is imperative to produce biodiesel by ultrasound. [7,8,9]

HYDRODYNAMIC CAVITATION:

Hydrodynamic cavitation involves the activity of the liquid bubble.It is a method in which cavitation is generated in the flow of liquid under restrained condition ,influenced by simple geometry and operating parameters.It is a method for easier generation of cavities and is also a cheaper alternative compared to the conventional process.Cavities are generated by hydrodynamic cavitation when a liquid is forced through a constriction resulting in pressure drop.As per Bernoulli's principle,velocity starts increasing due to reduced pressure.When the static pressure falls below the vapor pressure of the flowing liquid,cavities are formed which further collapse due to recovery of the pressure.This releases enormous amount of energy which helps in mitigating mass transfer limitation thereby improving the yield of biodiesel.The intensity of cavitation can be controlled by regulating operating conditions and optimizing geometric conditions.[5]

EFFECT OF OPERATING PARAMETERS:

EFFECT OF TYPE OF DIAMETER OF THE CONSTRICTION:

The diameter of the constriction affects the inception of cavitation. The cavitation number increases with an increase in the diameter of the hole. Thus for larger diameter holes, the cavitation starts at a higher cavitation number, thereby increasing the extent of the cavitation for the same cavitation number in the system resulting in a higher number of cavitation events occurring during the process and resulting in increase in biodiesel yield[9] using bubble dynamics simulations have clearly shown that, as the diameter of the hole increases, the collapse pressure generated for a single cavity also goes on increasing .It should be noted that the effect of diameter of hole studied by [10] was for a constant percentage free flow area occupied by the orifice holes and constant inlet pressure thereby maintaining a constant cavitation number in the system. Thus for the same free area, as we increase the diameter of the hole, the number of holes decreases, thereby decreasing the number of cavities generated. Thus optimization is needed on the basis of desired applications. So for intense cavitation,the diameter of the hole must be reduced and for reduced intensity the diameter of the hole must be increased. For hydrodynamic cavitation which has frequency less than 8 KHz, collapse pressure at the time of cavitation has an increment with reduction in frequency.Also, for constant free area,the frequency of turbulence reduces with an increase in the diameter of the hole.

EFFECT OF TYPE OF FREE AREA FOR THE FLOW:

The increment in the free area of the orifice results in low orifice velocity.When the flow rate is kept constant it results in a slower recovery of the pressure downstream of the orifice with an increase in the cavitation number. It should be noted that magnitude of the collapse pressure gets lowered during the cavity collapse and cavitation number rises with the fall in the orifice velocity resulting into a reduced number of cavities generated.This ultimately affects the biodiesel yield. The amount of pressure energy released will decrease with an increment in the free area available for the flow[7] have indicated that the collapse pressure generated by the collapse of cavities decreases with an increase in the percentage free area offered by the holes in the orifice plate

EFFECT OF TYPE OF INLET PRESSURE:

The collapse phase of cavitation phenomena depends on the rate of pressure recovery downstream of the constriction with respect to the final value and time of the recovered pressure.Energy dissipation rate also increases due to an increase in the permanent pressure drop across the orifice. So the collapse of the cavity becomes more rigorous which results in an increase in the pressure pulse generated at the collapse of the cavity. [12]has shown that the increase in the inlet pressure increases the cavitation number.Generation of cavities occurs mostly near the saturation vapor pressure of the liquid at the operating temperature. Increase in the inlet pressure, increases the throat pressure and decreases the cavity generation. Hence the cavitation number increases with an increase in the inlet pressure and the number of cavities generated decreases.This is due to choked cavitation where the downstream is completely filled with a large cavity cloud which escapes the liquid without collapsing giving reduced cavitational intensity and hence decreasing the biodiesel yield.

EFFECT OF TYPE OF CAVITATING DEVICE:

Geometrical parameters control the maximum size of the cavity, the number of cavities generated and the rate of collapse of a cavity[12] have studied the effect of type of cavitating device on biodiesel yield in interesterification reaction between WCO and methyl acetate was studied using different cavitating device such as orifice plate, circular and slit venturi under the fixed conditions of reactant mole ratio (1:12 of OMAMR), catalyst loading (1% by weight of oil) and inlet pressure of 3 bar . From the results it is been observed that biodiesel yield of 64% for the orifice plate, 82% for the circular and 89% for the slit venturi was obtained. The results indicate higher volumetric flow rate for a given pressure drop and lower cavitation number being obtained in slit venturi as compared to orifice plate and circular venturi. The number of cavitational events and the intensity increases with a decrease in cavitation number and these cavitational events are responsible for formation of local turbulence, liquid micro-circulation and micro-emulsion ultimately enhancing the biodiesel yield.It was reported that the slit venturi having a of 2.7, slit length to height ratio as 0.5 and a half angle of divergence section of 5.5 is an optimum geometry for the best cavitational activity as compared to circular venturi and orifice by Bashir.[4]The work done byMaddikerialso shows that higher biodiesel yield was obtained for the slit venturi as compared to the other two geometries. [12] It is also important to note here that the extent of increase in the final cavitational yield would also be dependent on the specific application. Overall it can be concluded that in the case of slit venturi, number of cavitational event are more as compared to orifice plate and circular venturi giving beneficial effects and hence it has been used as effective cavitating device .

EFFECT OF MOLE RATIO:

Molar ratio can influence the direction and biodiesel yield. Higher molar ratio favors forward reaction thereby increasing the yield. The molar ratio should be optimum such that the reaction time should be minimum with higher yield[12] studied the effect of oil to methyl acetate mole ratio(OMAMR) on biodiesel yield, experiments were conducted over the range of mole ratio from 1:10 to 1:14 by .As interesterification reaction is reversible in nature, higher oil to methyl acetate mole ratio favors the forward reaction for the production of desired product. The results indicate that the biodiesel yield increases from 83% to 89% with an increase in the mole ratio from 1:10 to 1:12. Using too much excess of reactants increases the load on separation and needs to be avoided. Casa reported the biodiesel yield of 76.7% at OMAMR of 1:50 using the conventional approach of only mechanical stirring which is lower than that obtained using hydrodynamic cavitation.[13]The intensification (both enhanced yield and lower requirement of excess reactants) are attributed to the cavitational effects of micro-emulsification and streaming.It should be also noted that using additional methanol although speeds up the reaction, it also increases the separation (methanol recovery) load on the system (only specific amount of methanol is required for actual reaction and hence any excess will appear as unreacted methanol thereby increasing the separation load) and hence an optimum operating ratio should be selected on the basis of overall economics and the equilibrium conversion.

EFFECT OF CATALYST CONCENTRATION:

Any use of excess catalyst with an objective of increasing reaction rates also increases the load on the catalyst separation process and hence understanding the effect of catalyst concentration is very important. The effect of potassium methoxide concentration on the biodiesel yields has been studied over a concentration range of 0.75–1.25% by Maddikeri[12] and it has been observed that an increase in the catalyst concentration from 0.75% to 1% results in increased biodiesel yield from 79% to 89%. The increase in the catalyst loading provides enhanced active sites for reaction giving higher conversion of triglycerides into biodiesel. However, a further increase in the catalyst concentration did not show any significant increase in the biodiesel yield and hence it was concluded that 1% catalyst loading is the optimum. [13] have investigated the interesterification reaction of sunflower oil and methyl acetate for biodiesel production and reported that a maximum conversion of 76.7% was obtained at an optimized catalyst loading of 1.04% by weight of the catalyst. The studies clearly establish the requirement of selecting optimum loading of catalyst.The concentration of catalyst should be kept optimum such that the conversion is higher with no additional cost or energy on the separation process.

ACOUSTIC CAVITATION:

Ultrasound is the sound waves having frequencies higher than those to which the human ear can respond which is greater than 16 kHz.The upper limit of ultrasonic frequency is about 5 MHz for gases and 500 MHz for liquids and solids. The uses of ultrasound within the large frequency range may be divided into two areas: low power, high frequency (1-10 MHz), which is the ultrasound normally used for medical diagnostics and chemical analysis; and high-power, low frequency (20-100 kHz), which is normally used for sanitation, polymer welding, and chemical reactions. The aim of high-power ultrasound is to cause a permanent chemical or physical change in a substance. To attain this, a high power intensity (1-1000 W/cm^2) is required. The energy released creates cavitation and microstreaming in liquids. The chemical effects of ultrasound do not arise from any explicit input of sonic energy to species at a molecular level, making the direct energy output insufficient to produce chemical reactions. High frequencies are dissipated faster than low frequencies. Higher the frequency of the ultrasound, higher is the requirement for initial intensity to satisfy an equivalent intensity at a congruent depth. Since the coupling of the sound field to the medium is imperfect, sonication induces molecular motion and this promotes efficient mass transfer and thus can enhance the rates of chemical reactions.[5]

EFFECT OF OPERATING PARAMETERS:

EFFECT OF MOLE RATIO:

Alcohol to oil mole ratio can affect the direction of the reaction and the yield of biodiesel in transesterification. The optimum alcohol to mole oil ratio is quite influenced by the system setup, reaction volume, catalyst (homogeneous or heterogeneous),operating pressure, etc. Concentration of alcohol in the reaction mixture will directly promote reaction rate. However, a fraction of alcohol would vaporize from the reaction vessel and cannot be involved in the chemical reaction until it is condensed back into the vessel by a condenser. This fraction is influenced by the temperature of the reaction.[Kelkar et al.,(2008)][Mootabadi et al.,(2010)][14] studied the esterification using 1:5 and 1:10 mole ratios of fatty acid(FA) to methanol with the quantity of concentrated sulphuric acid kept at a concentration of 1% by weight of the reactants under ultrasound. The results obtained exhibit a conversion of about 98% (mole) was achieved in 2 hour with a mole ratio of 1:10 and about 91% (mole) conversion was obtained in 3 hour for the operating mole ratio of 1:5. It should be tacit that using additional methanol although speeds up the reaction, it also increases the separation load on the system and only specific amount of alcohol is required for actual reaction and hence an optimum operating ratio should be selected on the basis of overall economics and the equilibrium conversion.[14,15]

EFFECT OF REACTION SPEED:

The use of ultrasound in the synthesis helps in reducing the reaction time significantly and obtaining higher yield. Mootabadiperformed the process where the reaction time was varied within a range from 10 min to 60 min for different catalyst at catalyst/oil mass ratio 3%, methanol/oil mole ratio 9:1 and ultrasonic power 50%, the improvements achieved by each of the catalyst were 75% for CaO, 47% for SrO and 30% for BaO catalysts after 60 min.[15] There is significant increase of biodiesel yield for all catalysts in the ultrasonic-assisted reactor. The magnitude of the improvement was higher at lower yields. At longer reaction time, the promotion of reverse reaction rendered the slower increase in yield with time. The promotional effect by ultrasonic energy was ascribed to the increase in interfacial area and activity of the microscopic and macroscopic bubbles formed when ultrasonic waves were applied to the three-phase reaction system. The catalysts could also last longer as new catalytic active sites could be exposed to the reactants due to the 'grinding' effects caused by the ultrasonic on the catalysts.

EFFECT OF REUSABILITY OF THE CATALYST:

The benefit of using ultrasound in the process is repeated use of the catalyst for improving the yield. But repeated use of catalyst ultimately results in the drop in the performance. The drop in the biodiesel yield due to the number of reuse of the catalysts could be due the deactivation of active sites due to their poisoning by some molecules present in the reaction mixture [15] A regeneration process could be applied to reverse the deactivation. In general there is a significant increase in the biodiesel yield for all catalysts in the ultrasonic-assisted systems as compared to the conventional magnetically stirred systems under the same reaction conditions.

EFFECT OF ULTRASONIC OUTPUT POWER:

Ultrasonic amplitude could influence the reaction rate and biodiesel yield as it is directly related with the power of the ultrasonic irradiation The effects of ultrasonic output power varying within a range of 25–100% by intervals of 25% were studied by Mootabadi[15] which showed that the most suitable amplitude for transesterification of palm oil using SrO as the solid base catalyst was 50%. A highest yield was achieved using 100% amplitude using BaO as the solid base catalyst and the most suitable amplitude for transesterification of palm oil using CaO as solid base catalyst was considered to be at 50%.When the intensity (i.e., ultrasonic power/irradiation area) is increased, the acoustic amplitude increases and a more violent collapse of the cavitation bubble will occur. The harsher the collapse of the cavitation bubble, the higher the jet velocity and micro-mixing at the phase boundary between the oil and methanol phases.This results in finer emulsion formation hence higher mass-transfer coefficient and thus higher biodiesel formation.

ANALOGY AND COMPARISON:

Acoustic cavitation is the result of passage of ultrasonic waves through the medium while hydrodynamic cavitation results from velocity variation in the flow due to the changing geometry of the path of flow such as an orifice or a throttling valve. In spite of this difference the mechanisms of generation of these two types of cavitation, the bubble behavior shows similar trends with the variation of parameters in both types of cavitation.The increase in the frequency of irradiation and reduction in the time of the pressure recovery results in an increment in the lifetime of the cavity whereas amplitudes of cavity oscillations increase with an increase in the intensity of irradiation and the recovery pressure and the rate of recovery. Thus it can be said that the intensity of ultrasound in the case of acoustic cavitation and the recovery pressure in the case of hydrodynamic cavitation are analogous to each other.The mole ratio beyond 1;12 not only increases the cost in acoustic cavitation but also leads to excess formation of alcohol which further creates difficulty in separation .Similarly,the frequency of the ultrasound and time or rate of pressure recovery are analogous to each other. Thus it is clear that the hydrodynamic cavitation can also be used for carrying out sonochemical transformations and the desired cavitation intensities can be obtained using proper geometric and operating conditions as discussed above.

It was reported that cavitating conditions identical to acoustic cavitation could be generated in hydrodynamic cavitation (HC), which even had a better effect on mixing immiscible liquids. The scale-up of hydrodynamic cavitation meets industrial-scale operations and has better opportunities than the ultrasonic reactor by reason of its easier generating and less sensitivity to the geometric details of the reactor.When it comes to power consumption,acoustic cavitation utilizes more energy compared to hydrodynamic cavitation but its proved to be much more effective in generating cavitation .

CONCLUSION:

For mitigating the mass transfer limitation during the reaction, cavitation is a excellent option compared to the conventional process .Cavitation can be effectively used for the synthesis of biodiesel with overall operation at ambient conditions of temperature and pressures as against the requirement of high pressures and reflux conditions for the conventional route of synthesis. Applicability of cavitation allows the flexibility in terms of raw material selection for possible lowering of the cost of production. Hydrodynamic cavitation can be effectively used for the intensification of the synthesis of biodiesel The micro level turbulence generated by the dynamic behavior of the cavitation bubbles assist in intensifying reaction by formation of a fine emulsion providing enhanced reaction area and turbulence which reduces the mass transfer resistance. The approach based on hydrodynamic cavitation gives intensified processing with higher biodiesel yield and also offers various improvements such as use of ambient conditions, requirement of lower excess of reactants and higher cavitation yield.

Ultrasonic and Hydrodynamic cavitation had a great enhancement effect on the synthesis of biodiesel. Both methods provide shorter reaction time and less energy consumption than the conventional mechanical stirring method. But Hydrodynamic mode of cavitation is more energy efficient and cheap as compared to the acoustic mode of cavitation. Hydrodynamic cavitation proved to be a potential method that could be used for biodiesel production at industrial scale due to its easy scale-up property.

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