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ASCENDANCY OF ULTRASONIC REACTOR FOR MICRO BIODIESEL PRODUCTION

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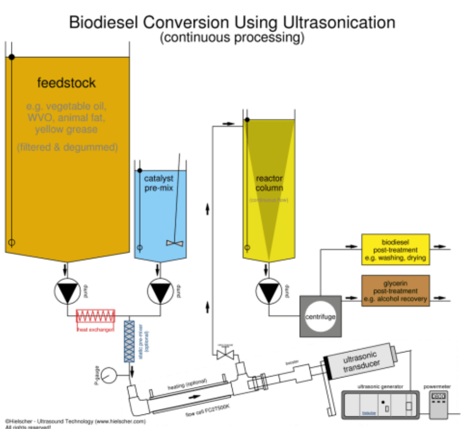
Graphical abstract



Abstract

Biodiesel is a form of biofuel; diesel fuel manufactured from vegetable oils, animal fats, or recycled greases. Biodiesel is produced through a process called transesterification which involves taking naturally occurring carbon chain molecules, known as triglycerides, found in such feed stocks as seed oils and animal fats, and converting them into methyl esters, which is the chemical term for biodiesel. The conventional transesterification of the triglycerides to fatty methyl esters and glycerin is slow and not complete. During the conversion process not all fatty acid chains are turned into alkyl esters (biodiesel) reducing biodiesel quality and yield, significantly. In considering a new biodiesel facility or an upgrade of existing biodiesel plant, it is imperative that ultrasonic mixing technology be considered; it is efficient and ideal for micro scale biodiesel processing. This paper infers the efficiency of Ultrasonics for the ultrasonication of liquids and gleans that Ultrasonic cavitational mixing is the most advanced means to form fine-size emulsions at micro processing scale. The paper construes the innovative ascendancy of 'Ultrasonic Reactor' for micro scale production of biodiesel and demonstrates that there is a direct link between methanol droplet size, biodiesel yield, and conversion speed which makes ultrasonic reactors the most productive technology in the biodiesel industry. The paper concludes that biofuels are sustainable alternative to fossil fuels and biodiesel is a green energy source for agriculture, transport and power generation at micro level use in rural communities.

Keywords: Biodiesel, biofuels, green energy, transesterification, ultrasonics, ultrasonic reactor

1.0 INTRODUCTION

When the world oil prices briefly shot up to nearly $ 150 per barrel in the summer of 2008, the global economy shuddered and swooned. Thus began the worst recession since 1930. Of course other factors contributed to the crash; most notably, a bursting housing bubble in the United States and an unsustainable build-up of debt in nearly all the world's industrial economies. But it is clear both that high oil prices added to financial instability, and the oil price spike of 2008 provided a sudden gust that helped bring down the house of cards. Evidence that climate change is real and caused by human activity has become irrefutable, and serious climate impacts (such as the melting of Arctic ice cap) have begun appearing sooner, and with greater severity, than had been forecast.

Climate change is not just an environmental issue; it touches every part of our lives: peace, security, human rights, poverty, hunger, health, mass migration and economics. It is a global issue and it calls for global action. To be able to discuss energy as a separate matter is an intellectual illusion. The CO_2 emissions are not the only problem of fossil energy. The radioactive contamination is not the only problem of atomic power. Many other dangers are caused by using atomic and fossil energies: from polluted cities to the erosion of rural areas; from water pollution to desertification; from mass migration to overcrowded settlements and the declining security of individuals and states. Because the present energy system lies at the root of these problems, renewables are the solution to these problems. Increasing environmental concerns and the need for energy independence have led to the biofuels including the biodiesel market; source of renewable energy.

Renewable energy sources, in power generation as well as in transport, continued to increase in 2013; reaching a record 2.7% of global energy consumption, up from 0.8% a decade ago. Renewable energy used in power generation grew by 16.3% and accounted for a record 5.3% of global power generation. China recorded the largest incremental growth in renewables, followed by the US, while growth in Europe's leading players – Germany, Spain and Italy – was below average. Globally, wind energy (+20.7%) once again accounted for more than half of renewable power generation growth and solar power generation grew even more rapidly (+33%), but from a smaller base. Global biofuels production grew by a below-average 6.1% (80,000 b/d –oil equivalent), driven by increases in the two largest producers: Brazil (+16.8%) and the US (+4.6%) [1].

Biodiesel is the main biofuel for transport used in the EU and accounted for about 70 percent of the biofuels market on volume basis in 2012. Despite the economic recession, global biofuels output reached 120 billion litres in 2013 and now provides 3.5% of world transport fuel demand. Global biofuels output is estimated to grow at 3.5% per year on average from 110 billion litres in 2012 to 135 billion litres in 2018 and to provide 4% of global road transport fuel demand in 2018 [2]. The biodiesel market grew from $8.6 billion in 2009 to $12.6 billion in 2014. Market growth is primarily dependent on the availability, quality, and yield of feedstock, as it accounts for 65% to 70% of the cost of biodiesel production. Biodiesel production was 29.1 million tons in 2014; Asia accounted for 18% of global biodiesel production in 2014, the majority from palm oil in Indonesia, Malaysia and Thailand [3, 4]. In 2010, Neste Oil opened up a renewable diesel plant in Singapore with an annual capacity of 800,000 MT and a similar plant in Rotterdam in 2011. Since 2012, the Neste plants were operating at nearly full capacity and refined 1.36 MMT of palm oil, 0.74 MMT of waste and residues and 7,000 MT of other vegetable oils.

World is looking up to mega energy projects for solutions whereas the resolution lies in the opposite direction; micro energy at the local community level. Papworth (2011) [5] quotes Leopold Kohr's argument that "there seems to be only one cause behind all forms of social misery: Bigness. It appears to be the one and only problem permeating all creation. Whenever something is wrong, something is too big. And if the body of a people becomes diseased with the fever of aggression, brutality, collectivism, or massive idiocy, it is not because it has fallen victim to bad leadership or mental derangement. It is because human beings, so charming as individuals or in small aggregations, have been welded into over concentrated social units [6]. That is why: *The Fourth World;* the world of small nations, small communities and small enterprises is the only world that can be democratic and reflect genuine human needs or desires. The only way forward is to: promote *Microenterprise;* in *Short Supply Chain;* using *Appropriate Technology;* working towards *Right Livelihoods;* incorporating *Human Scale Development;* by giving due rights to the *Invisibles;* and, in planning, populations are measured in terms of *Ecosons* [7].

The term *microenterprise* connotes different entities and sectors depending on the country. Generally speaking;

in developed countries, microenterprises comprise the smallest end (by size) of the small business sector, whereas in developing countries, microenterprises comprise the vast majority of the small business sector; a result of the relative lack of formal sector jobs available for the poor. Micro and Home Business Network, an Australian organization, defines a micro-business as one with five or less employees. This definition is often used in the United States. In Europe a business with less than ten employees may be officially considered a micro-business. Microenterprises add value to a country's economy by creating jobs, enhancing income, strengthening purchasing power, lowering costs and adding business convenience [8].

2.0 MICRO BIODIESEL PRODUCTION

First, it's important to understand that even though diesel is part of its name, pure biodiesel does not contain petroleum diesel or fossil fuel of any kind. Biodiesel is a biofuel: a subcategory of biomass that includes three energy-crop-derived liquid fuels; ethanol (referred to as grain alcohol), methanol (referred to as wood alcohol), and biodiesel. Technically, a fatty acid alkyl ester, biodiesel can be easily made through a simple chemical process from virtually any vegetable oil including; Soy, Palm, Corn, Canola, Coconut, Jatropha, Millettia Pinnata, Cotton seed, Peanut, Sunflower and many more. Biodiesel can also be made from recycled cooking oil or animal fats from rendering plants. There have been some promising experiments with the use of algae as a biodiesel feed stock. Biodiesel is most commonly produced through a process called transesterification (Figure: 1) which involves taking naturally occurring carbon chain molecules, known as triglycerides, found in such feed stocks as seed oils and animal fats, and converting them into methyl esters, which is the chemical term for biodiesel.

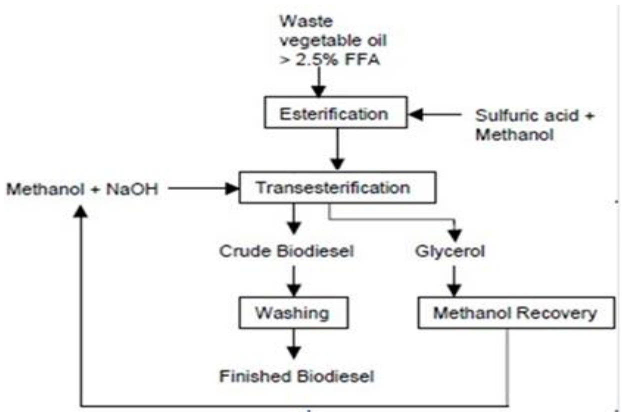


Figure 1 Biodiesel production flow chart (Source: ESRU, 2013)

Almost all biodiesel is produced using base catalysed transesterification as it is the most economical process requiring only low temperatures and pressures and producing a 98% conversion yield. The Transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the glycerine. The nature of the fatty acids can in turn affect the characteristics of the biodiesel. During the esterification process, the triglyceride reacts with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalysed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production; either base can be used for the methyl ester. Figure 2 shows the chemical process for methyl ester biodiesel. The reaction between the fat or oil and the alcohol is a reversible reaction and so the alcohol must be added in excess to drive the reaction towards the right propensity and ensure complete conversion [9].

The approximate proportions of the reaction are:
100 lbs of oil + 10 lbs of methanol → 100 lbs of biodiesel + 10 lbs of glycerol

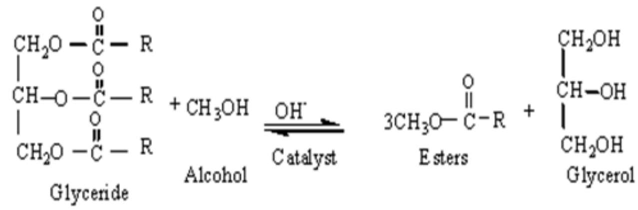


Figure 2 Chemical process for methyl ester biodiesel (Source: ESRU, 2013)

Once separated from the glycerin, the biodiesel goes through a purification process, removing all remaining alcohol and catalyst. It is then dried and stored. To guarantee the biodiesel is without color, odor and Sulphur, an additional distillation process may be implemented.

Soybean oil is the most common feedstock used in U.S. production, while rape seed and palm oil is used in Europe and Asia. An important factor in considering which feedstock to use is the stock's free fatty acid (FFA) content. Biodiesel is a low-emissions diesel substitute fuel made from renewable resources and waste lipid. The most common way to produce biodiesel is through transesterification, especially alkali-catalyzed transesterification; it is safe, biodegradable, and produces less air pollutants than petro diesel. Biodiesel can be used in its pure form (B100) or blended with petroleum diesel; common blends include B2 (2% biodiesel), B5, B10, and B20. Most vehicle manufacturers approve blends up to B5, and some approve blends up to B20. In considering a new biodiesel facility or an upgrade of existing biodiesel plant, it is imperative that ultrasonic mixing technology be considered; it is efficient and ideal for micro scale biodiesel processing. Biodiesel must be segregated and handled separately because of its unique physical properties. Biodiesel can be corrosive to rubber materials and liner materials and cannot be stored in concrete lined tanks [10, 11].

2.1 Biodiesel Quality

Today, making biodiesel is not just about making a renewable fuel; for biodiesel producers this is the challenge of producing high-quality biodiesel with consistent characteristics, regardless of feedstock at times. Using traditional ASTM (American Society for Testing and Materials) methods is time consuming and challenging. It involves sample preparation, the use of reagents, and time; usually at least 40 minutes per sample. Quality Trait Analysis (QTA) offers an Infra-red based, on line, quality testing system for biodiesel producers. Besides its potent user-interface, QTA offers gamut of options; from measuring the feed stocks & raw materials, in process fuel, and glycerin purity to finished B100 per ASTM D6751 & EN14214 specs [12].

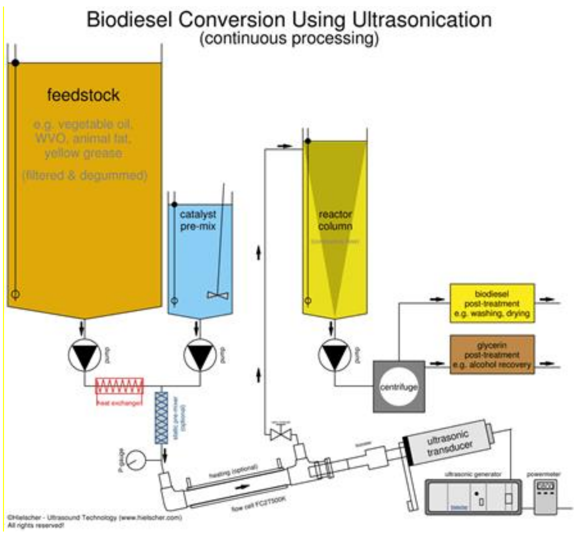


Figure 3 Biodiesel conversion using ultrasonication (Source: Hielscher Ultrasonics)

3.0 ASCENDANCY OF ULTRASONIC REACTOR

3.1 Ultrasonics

Ultrasonics specializes in equipment for the ultrasonication of liquids (Figure: 3); this includes homogenizing, disintegration, emulsification, and dispersing or particle size reduction (milling). Ultrasonication is an effective means to break cell structures; it generates alternating high-pressure and low-pressure waves in the exposed liquid. During the low-pressure cycle, the ultrasonic waves create small vacuum bubbles in the liquid that collapse violently during a high-pressure cycle. This phenomenon is termed as ultrasonic Cavitation. Ultrasonic waves of high intensity ultrasound generate cavitation in liquids. Cavitation causes extreme effects locally, such as liquid jets of up to 1000 km/hr, pressures of up to 2000 atm (29,400 psi) and temperatures of up to 5000 Kelvin (4727 C^0). The implosion of the cavitation bubbles results in micro-turbulences and micro-jets of up to 1000km/hr. Large particles are subject to surface erosion (via cavitation collapse in the surrounding liquid) or particle size reduction (due to fission through inter-particle collision or the collapse of cavitation bubbles formed on the surface). This leads to sharp acceleration of diffusion, mass-transfer processes and solid phase reactions due to crystallite size and structure changing. The implosion of the cavitation bubble causes strong hydrodynamic shear-forces. These shear forces can disintegrate fibrous, cellulosic material into fine particles and break the walls of the cell structure, releasing more of the intra-cellular material, such as starch or sugar into the liquid. In addition, the cell wall material is being broken into small debris. Cavitation is an extraordinary method of concentrating the diffuse energy of sound into a chemically usable form [13].

3.2 Ultrasonic Homogenizing

Ultrasonic homogenizing is a mechanical process to reduce small particles in a liquid so that they become uniformly small and evenly distributed; it is very efficient for the reduction of soft and hard particles. The homogenization is based on cavitation. When liquids are exposed to intense ultrasonication, sound waves propagate through the liquid causing alternating high-pressure and low-pressure cycles (approx. 20000 cycles per sec). During the low-pressure cycle, high-intensity small vacuum bubbles are created in the liquid, as the liquid vapor pressure is attained. When the bubbles reach a certain size, they collapse violently during a high-pressure cycle. During this implosion very high pressures and high speed liquid jets are generated locally. The resulting currents and turbulences disrupt particle agglomerates and lead to violent collisions between individual particles (Figure: 4).

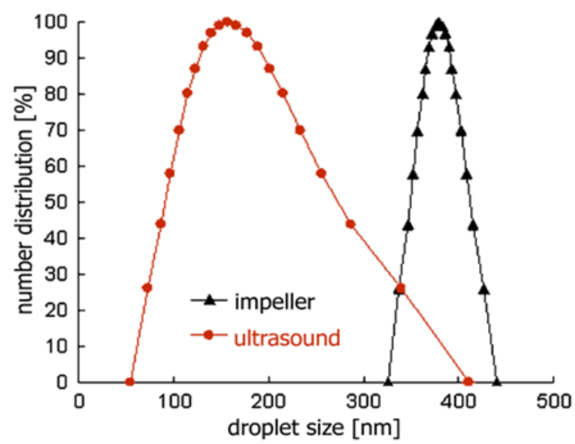


Figure 4 Comparative droplet size

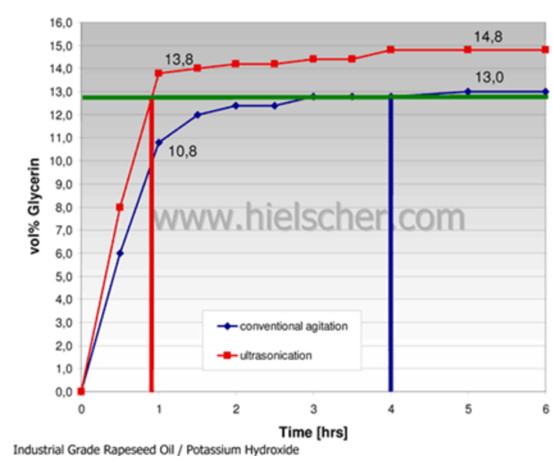


Figure 5 Comparative agitation

3.3 Emulsions

Emulsions are dispersions of two or more immiscible liquids. Highly intensive ultrasound supplies the power needed to disperse a liquid phase (dispersed phase) in small droplets in a second phase (continuous phase). In the dispersing zone, imploding cavitation bubbles cause intensive shock waves in the surrounding liquid and result in the formation of liquid jets of high liquid velocity. In order to stabilize the newly formed droplets of the disperse phase against coalescence, emulsifiers (surface active substances, surfactants) and stabilizers are added to the emulsion. As coalescence of the droplets after disruption influences the final droplet size distribution, efficiently stabilizing emulsifiers are used to maintain the final droplet size distribution at a level that is equal to the distribution immediately after the droplet disruption in the ultrasonic dispersing zone. Stabilizers actually lead to improved droplet disruption at constant energy density (Figure: 5).

3.4 Dispersing (Milling) and De-Agglomeration

Dispersing (Milling) and de-agglomeration of solids into liquids is another important application of ultrasonic devices. Ultrasonic cavitation generates high shear that breaks particle agglomerates into single dispersed particles. High intensity ultrasonication is an interesting alternative to other technologies such as; high pressure homogenizers, agitator bead mills, impinging jet mills and rotor-stator-mixers. When sonicating liquids the sound waves that propagate into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. This applies mechanical stress on the attracting electrostatic forces. Ultrasonic cavitation in liquids causes high speed liquid jets of up to 1000km/h (approx. 600mph). Such jets press liquid at high pressure between the particles and separate them from each other. Smaller particles are accelerated with the liquid jets and collide at high speeds. This makes ultrasound an effective means for the dispersing and de-agglomeration but also for the milling and fine grinding of micron-size and sub-micron size particles.

3.5 Sonochemistry

Sonochemistry is a branch of chemical research dealing with the chemical effects and applications of ultrasonic waves; that is, sound with frequencies above 20 kHz those lie beyond the upper limit of human hearing. Sonochemistry is the application of ultrasound to chemical reactions and processes. The mechanism causing sonochemical effects in liquids is the phenomenon of acoustic cavitation, explained earlier. Sonochemistry - is applied to enhance the mass-transfer in the production of biodiesel [13].

Figure 6 Ultrasonic Reactors; UIP 500, 1000 &1500hd models (Hielscher Ultrasonics)

3.6 Ultrasonic Reactors

Ultrasonic Reactors are recommended for biodiesel production capacities of 0.25 ton (80 gal) per hour or more (Figure 6). In general, production/operation should consider using three to five units in parallel to accommodate variations in production rates. Excess methanol and catalyst are significant cost factors in biodiesel production. Hielscher ultrasonic reactors add cavitational shear to the mixing process. This gives much smaller methanol droplets resulting in improved methanol and catalyst utilization. Therefore, less methanol and catalyst are required. In addition to that, the cavitation influences the reaction kinetics, leading to faster and more complete transesterification. Ultrasonic mixing reactors replace tank agitators and other dynamic shear mixers. The ultrasonic reactors are generally installed to mix two feed streams; oil and methanol (with catalyst). For this, crude pre-mix is pumped into the ultrasonic reactor, where the ultrasonic cavitation mixes and emulsifies both reagents within 5 to 15 seconds. This is an inline mixing process. When the mix exits the flow cell reactor, the glycerin will separate by gravity within less than 60 minutes. Alternatively, one can feed the mix into a centrifuge after several minutes of residence / reaction time. The inline mixing reduces the number and volume of tanks used for conventional batch processing. This improves capital utilization.

Basically, making biodiesel from oil, methanol (or ethanol) and catalyst, is a simple chemical process. The problem lies in the chemical reaction kinetics. The conventional transesterification of the triglycerides to fatty methyl esters (FAME) and glycerin is slow and not complete. During the conversion process not all fatty acid chains are turned into alkyl esters (biodiesel). This reduces the biodiesel quality and yield, significantly.

The long conversion time and the inferior biodiesel yield can be attributed, to a large part, to the use of inappropriate mixing systems. In principle, oil and methanol are immiscible; therefore; a methanol-in-oil emulsion needs to be formed. This requires emulsification equipment rather than conventional mixers or stirrers. Ultrasonic cavitational mixing is the most advanced means to form fine-size emulsions at micro and large processing scale.

There is a direct link between methanol droplet size and biodiesel yield as well as conversion speed. This makes ultrasonic reactors the most productive technology in the biodiesel industry; biodiesel conversion process using Ultrasonication is shown in figure 3. The ultrasonic mixing devices produce more high quality biodiesel, faster. The installation of ultrasonic reactors into the biodiesel process line reduces operational costs, too. Excess methanol does not react during the conversion process. It is added to support the chemical reaction kinetics only and it needs to be recovered at the end of the process. Recovered methanol is of inferior quality, only; that is why methanol recovery increases your processing costs. The use of ultrasonic reactors reduces the required amount of excess methanol by up to 50%. A molar ratio (The mass of a mole is the gram formula mass of a substance) between 1:4 or 1:4.5 (oil: methanol) is sufficient for most feedstock, when using Hielscher ultrasonic mixing.

Many biodiesel producers - in particular small and mid-size community level biodiesel producers - reduce their costs by switching to raw materials of poorer quality, such as animal fats, recycled restaurant oils or waste oils. The ultrasonic process intensification improves the conversion results for any feedstock. This makes it easier to produce ASTM D6751or European EN 14212 compliant biodiesel from high FFA oil or high viscosity fat or grease.

Catalyst price represents a marginal fraction of the biodiesel production costs only. As with the excess methanol, the costs result from recovery and inferior glycerin quality. Ultrasonic mixing improves the methanol-in-oil emulsification and generates more and smaller droplets.

This leads to a better distribution and increased catalyst efficiency. In addition to that, the ultrasonic cavitation improves the mass-transfer; as a consequence, you can save up to 50% catalyst when compared with shear mixers or stirrers.

Glycerin is a byproduct of biodiesel production. A higher conversion rate and lower excess methanol lead to a much faster chemical conversion and to a sharper separation of the glycerin. For the reasons described above, the glycerin contains less catalyst or mono-glycerides and it causes lower refining costs. Biodiesel is a green fuel. To be green, the energy required for growing, harvesting and processing must be lower than the energy contained in the biodiesel. The installation of ultrasonic mixing lowers the energy required for processing. Hielscher ultrasonic devices have an outstanding efficiency in the conversion of electricity to mechanical mixing action. These ultrasonic devices process approx. 22 gallon of biodiesel using only 0.1kWhr electricity, which is equivalent to operating a 100 watts light bulb for one hour. This is a fraction of the energy consumption of shear mixers or hydro-dynamic mixers.

The ultrasonically assisted transesterification can typically run at lower process temperatures; this reduces the required heating energy, as well.

In a US study two 1 kW ultrasonic reactors, model UIP1000hd from Hielscher, were used in converting a 500 gallon batch biodiesel process to a continuous process with a proposed design flow rate of 1-2 GPM (gallons per minute). The reactors were installed in a privately designed and owned biodiesel plant using PBSY (*Prime Bleachable Summer Yellow*) cottonseed oil. Changes in operational parameters were tested, over two months, to determine performance impacts including; vegetable oil flow rate, methanol to oil ratio, catalyst to oil ratio, reactor inlet temperature and reactor pressure. The study of these reactors provided the facility operators with the following conclusions: The use of Hielscher ultrasonic reactor technology is a highly cost-effective means of converting a batch biodiesel reaction process to a continuous process; High quality biodiesel can be produced on a continuous basis with greatly reduced operating costs in terms of methanol and catalyst usage; The ultrasonic reactors provide significant operational flexibility; and key operating parameters may be easily adjusted to optimize process performance with the aim of continuous control of biodiesel quality [14].

4.0 CONCLUSION

Biodiesel, a form of biofuel, is a green fuel; diesel fuel manufactured from vegetable oils, animal fats, or recycled greases. It is safe, biodegradable, and produces less air pollutants than petroleum-based diesel. It is part of the solution to make the energy supply more renewable and will pave the way for a cleaner environment and creation of jobs. Ultrasonic reactor technology is highly cost effective way to micro produce biodiesel. The ultrasonic process intensification considerably improves the conversion rate with lower excess methanol, making it easier to produce biodiesel to ASTM D6751 and EN 14212 specifications.

The impact of growing biofuels markets has the potential to provide new jobs and incomes throughout the supply chain from rural communities and farmers to biotechnology and engineering companies, and fuel producers and distributors across the world. The EU, the US, South America, emerging economies and developing nations, can all potentially benefit from the development of sustainable advanced biofuels, in particular, biodiesel. Renewable energies can stimulate technological innovation and economic development, and that renewable energy will become fully competitive with conventional energy systems. Renewable energy has crucial economic and social benefits for the poorest countries in the world; home grown renewable sources can help developing countries to fuel their economic development and to insulate themselves against rising world energy prices.

The phrase "Think globally, act locally" urges people to consider the health of the entire planet and to take action in their own communities and cities. In fact it is small villages and towns that are driving the move toward 100 percent renewable energy policy in Germany; German villages compete with each other for the title of who produces more renewable energy per capita. Winners are even feted with an annual award. The incentive to use 100% renewable energy, for electricity, transport, or even total primary energy supply globally, has been motivated by global warming and other ecological as well as economic concerns. Renewable energy use has grown much faster than anyone anticipated [15].

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