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Commentary

Synergism of microwaves and ultrasound for advanced biorefineries

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Abstract

Conventional energy sources are limited and non-renewable and their consumption contributes to greenhouse gas emissions. The world is in need of advanced biorefineries to meet ever growing energy demands associated with population growth and economic development. An advanced biorefinery should use renewable and sustainable (both in quality and quantity) feedstock that gives rise to higher energy gains with minimum non-renewable energy and resource consumption. Development of advanced biorefineries is currently encircled by two major issues. The first issue is to ensure adequate biofuel feedstock supplies while the second issue is to develop resource-efficient technologies for the feedstock conversion to maximize energy and economic and environmental benefits. While microalgae, microbial derived oils, and agricultural biomass and other energy crops show great potential for meeting current energy demands in a sustainable manner, process intensification and associated synergism can improve the resource utilization efficiency. Synergism of process intensification tools is important to increase energy efficiency, reduce chemical utilization and associated environmental impacts, and finally process economics. Among the many process intensification methods, this commentary provides a perspective on the essential role of MWs and US and their synergy in biofuel production. Individual, sequential, and simultaneous applications of MWs and US irradiations can be utilized for process intensification of various biofuels production and selective recovery of high value bioproducts. Process related barriers, namely mass and heat transfer limitations, can be eliminated by this synergism while improving the reaction efficiency and overall process economics significantly. In this article, a brief review focused on recent developments in MW and US mediated process intensification for biofuel synthesis and associated issues in their synergism followed by a discussion on current challenges and future prospective is presented.

Keywords: Microwave and ultrasound; Process intensification; Green chemistry; Resource utilization; Biorefinery

1. Introduction

The world's oil, natural gas, and coal reserves were reported as 1700 billion barrels, 187.1 trillion cubic meters, and 891.5 billion tons, respectively, in 2014, adequate to meet the world's consumption at the current rate for 52.5 years, 54.1 years and 110 years respectively [1]. On the other hand, global consumption increased for all fuels, reaching record levels for every fuel type except nuclear power; production increased for all fuels except coal. The renewable energy production increased by 12%, accounting for 6% of the global power generation (or 3% global electricity consumption). Meanwhile, world biofuel production increased by 7.4% (nearly 5 million tons oil equivalent). Global ethanol production increased by 6.0%, led by production increases from North America (USA – 5.6%), South (Argentina – 30.9%; Brazil – 5.5%) and Central America, and Asia Pacific (Indonesia – 40.4%), while biodiesel production increased by 10.3% despite a decline in production in North America [1].

Escalating environmental pollution associated with fossil fuel consumption has created an urge for nations around the world to investigate into renewable and sustainable energy and fuel supplies such as biofuels. The stimulus for research in biofuel synthesis comes from their additional benefits of high energy density (e.g., energy density for biodiesel is higher than compressed natural gas or gasoline with 10% ethanol or 100% ethanol [2]), high capacity factor (e.g., resource availability for biomass is higher than solar and wind sources [3]) and ease in process utilization. However, current biofuel industry is encircled by two major issues. First, ensuring adequate biofuel (biomass-derived) feedstock supplies that can make significant

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contributions toward the total global energy load (~10 TW) generated by the fossil fuel sources [4], and the second is to address the first without adverse environmental impacts by efficient resource utilization, and produce biofuels without causing energy–food–environment trilemma.

Various types of biofuel feedstock were utilized for biofuel production which include vegetable plants, oil seed crops (edible such as peanut, soybean, and corn), seeds known as first generation feedstock; animal fats, non-edible oils (jatropha, Karanja and other tropical oil seeds), waste oils, lignocellulosic feedstock, grass, crop residues and waste biomass called second generation feedstock; and more recently algae, cyanobacteria and microbial (from wastewater sludge) oils called third generation feedstock [5]. Considering the escalating demands for the transportation and other fuels for various industrial uses, algae and other low cost feedstock seem to be the most promising and reliable feedstock since it has the potential to sustain the biofuel production at current consumption and meet the process economics by delivering valuable bioproducts. Algae have the potential to produce up to 200 times more oil per hectare annually when compared to other terrestrial oil crops [6,7]. Apart from ensuring adequate feedstock supplies for biofuel production, another major hurdle lies in their conversion processes [5]. Conventional and ambient pressure or high pressure and high temperature processing methods are not chemical- or energy-efficient or even cost-effective. In this context, process intensification has gained increasing interest in conventional and emerging chemical industries. Process intensification also became an essential endeavor in conventional petroleum and other oil refining industries to improve the energy and material utilization efficiencies [8]. Process intensification and the synergism promoted by its effects can lead to the development of resource-efficient technologies [9]. This article describes the benefits of process intensification and its synergism for the development of resource-efficient technologies. Microwaves (MW) and ultrasound (US) have been discussed as two potential novel and unique process intensification methods for developing resource-efficient advanced biorefineries.

2. Resource efficient technologies for biorefineries

To reduce the energy and material utilization inefficiencies and increase economic and environmental benefits, resource-efficient technologies should be developed. Process intensification and associated synergistic effects may help develop resource-efficient technologies for biorefineries. Process intensification refers to the development of novel equipment and/or methods that produce significantly higher yields or superior benefits in comparison with the existing equipment and/or methods in practice. These benefits can be realized in the form of dramatic reduction in processing times, significant improvements in product quality or quantity and decreasing the equipment size, reducing the complexity of production schemes, improving the energy efficiency, minimizing the waste production, and finally resulting in cheaper, safer and sustainable technologies [10]. The process intensification developments in *equipment* could focus on developing novel reactor design with intense mixing to promote heat- and mass-transfer while the developments in *methods* could focus on integrating the reaction–separation processes (minimizing process steps), use of alternative energy sources, and new process control techniques. For example, in the context of biodiesel production, process intensification efforts refer to the increasing mass and heat transfer rates among the reaction products whether in extraction and/or transesterification and/or separation and/or purification stages.

2.1. Synergism by process intensification

Process intensification by combining two individual process tools or mechanisms may lead to synergism (magnified impact) [9]. Synergism can be defined as a phenomenon resulting from the effect of a combination of technologies, tools, or reagents that exceed the sum of their individual effects [11]. To achieve synergism, process intensification should successfully address the following major criteria [12]: (i) maximize the effectiveness of intramolecular and intermolecular interactions by creating dynamic conditions to promote kinetic regimes with higher conversion and efficiency; (ii) ensure uniform gradient-less mixing and heating; (iii) optimize driving forces and maximizing specific surface areas to improve the heat and mass transfer; and (iv) maximize the synergistic effects from conventional or partial processes.

The most relevant issues addressed by process intensification are structure (in molecular reactions, catalysis), energy (thermodynamic domain in which energy is imparted to the chemistry, hydrodynamic and transport processes), synergy (functional domain in multi-functional tools developed) and time (temporal domain in which timing of events, application of dynamics and process control) [13]. However, it is important to identify suitable process configurations when combining two conventional process effects to promote process intensification and thereby synergy among them. It is often realized as a process related issue [9]. All process combinations may not result in process intensification. Even if they provide a synergism, several additional issues may arise from the novel processes with regard to process control and optimization.

2.2. Synergism of microwaves and ultrasound

MW or US mediated organic synthesis has been the focal point in recent years mainly due to the superior effects in shorter reaction times and high product yields [5]. While these two process intensification effects have been well utilized in various process chemistry and engineering applications, biofuel industry has yet to explore their beneficial characteristics more extensively. These two non-conventional irradiation processes have been utilized in feedstock preparation, pretreatment, extraction, chemical conversion, and post-treatment stages of biofuel production [14]. However, the synergism of the two effects has not been explored much.

MWs deliver an effect generated by the electromagnetic interaction with reaction materials often resulting in thermal enhancement that produces superior results in chemical synthesis (Fig. 1a) [15]. MWs are capable of providing instant process heat resulting from three major mechanisms in a reaction

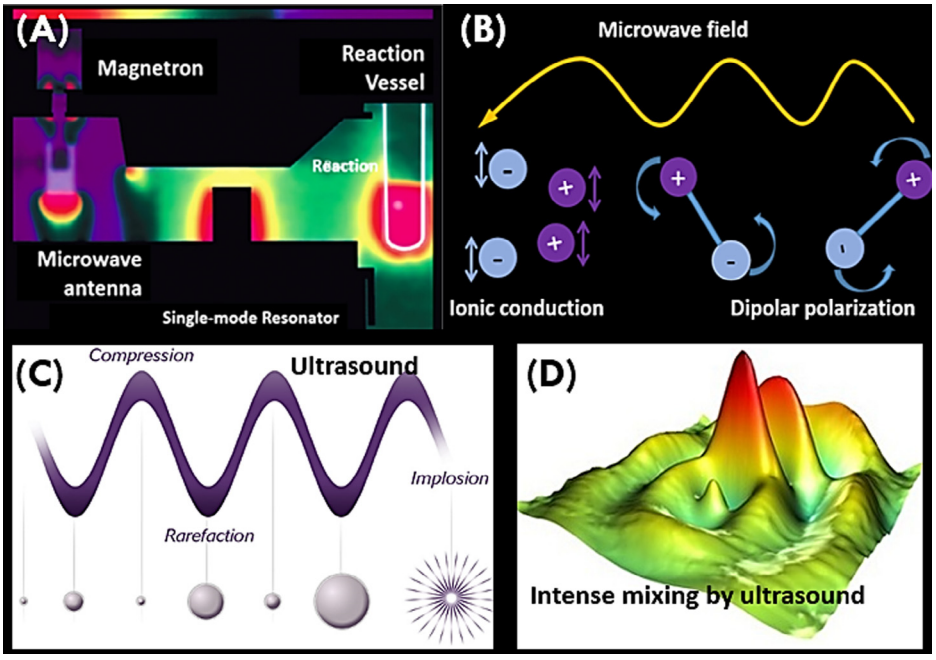

Fig. 1. (a) A single-mode resonator MW unit and MW energy dissipation in a lab-scale reaction vessel; (b) causes of MW effects through ionic conduction and dipolar polarization; (c) compression and rarefaction cycles, associated bubble growth and collapse induced by the US irradiation; and (d) the intense mixing effect by the US in a reaction environment.

environment. Ionic conduction, dipolar momentum and interfacial polarization (a combination of ionic conduction and dipolar momentum) are the major causes for this rapid heating (Fig. 1b) [14]. US are the acoustic cavitations generated by interaction of the sound waves (Fig. 1c) with the reaction compounds resulting in intense mixing (Fig. 1d) which increases the mass and heat transfer among the reaction mixtures leading to higher process efficiency [16,17]. For example, process intensification by US can promote mass transfer among gas and liquid components by up to five-fold while the liquid–solid mass transfer can be increased by 20–25 fold and increase product yields significantly (Fig. 2). The reaction times can be drastically reduced by MW heating by up to 1250 times due to rapid heat

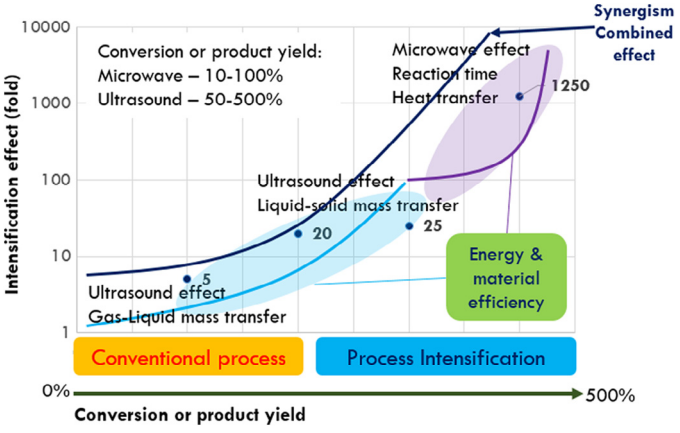

Fig. 2. Process intensification effects by MWs (electromagnetic field) and US (cavitation field): energy and material efficiency are the potential sustainability effects.

enhancement [13]. These two irradiations can also improve the energy and material efficiencies due to higher product conversion and yields.

Although MWs provide for rapid heating of the reaction materials, mass transfer of the reaction medium is often compromised in these reactors [11]. In addition, they interact with reaction materials at a higher rate which results in hot spot formation and thermal runaway. This phenomenon clearly indicates the necessity for a mixing mechanism which can ensure uniform heating of reaction materials and mass transfer promoted by the unusual heating advantage of the MWs. In a similar context, US is capable of promoting heat and mass transfer within the reaction medium due to the intense mixing they provide as a result of the acoustic cavitations which form microbubbles with air. The formation–release–collapse of these microbubbles provides cooling and heating cycles at microscales accompanied by high thermal and pressure release. Since this energy release is at micro levels, this energy is not adequate to cause high temperature gains in the reaction medium which depends on the time of exposure, reactor volume and the type of reaction. This clearly presents a limitation for US mediated reactions [11]. These reactions require external heating to enhance the process kinetics.

Considering the aforementioned prospects and limitations for the individual process intensification mechanisms, it is convenient to design a hybrid system that incorporates both non-conventional heating and mixing effects that may lead to enhanced process outcomes. This might lead to greener chemistry since efficient use of chemicals, energy and materials can be anticipated [11,18,19]. Superior benefits gained through the integrated process intensification effects might prove to be

economical at large scale applications. It is important to note that this hybrid technology will prove to be ideal for production of high value bioproducts combined with biofuels at present.

MW and US based chemical reactions have been reported to utilize lower amounts of catalysts and solvents along with lower energy consumption in chemical (both organic and inorganic) synthesis. Above all, the reaction times are dramatically decreased (reaction kinetics increased) and the product recovery is greatly enhanced [5,17–22]. These facts clearly support the fundamental principles of green chemistry which refer to *atom economy* and *e-factor* [18]. Atom economy refers to the efficient utilization of the raw materials employed in a reaction (maximizing conversion of desired atoms the reactants into desired products), i.e., converting the raw materials into desired or useful products. The e-factor refers to the amount of waste generated in the process of delivering a desired product. The lower is the e-factor, the greener is the reaction or process. Eliminating waste emissions is the key to accomplishing resource-efficient chemical processes and sustainable biofuel process development.

3. MW and US based advanced biorefinery

Researchers around the world have investigated the beneficial aspects of MWs and US and accounted for their process intensification benefits in numerous studies. Apart from the pharmaceutical, chemical, and industrial applications, MWs and USs have been extensively used and equally investigated for their benefits in biofuel synthesis and bioproduct recovery from various feedstock ever since their discovery. MWs and US can influence the production of bioethanol, biodiesel and biogas which are the three major energy carriers in use today. In addition to these energy carriers, MW and US irradiations can be utilized either in sequential or simultaneous pattern for efficient and selective recovery of various high value bioproducts. Sequential application facilitates process intensification while simultaneous application provides a unique synergy that enhances process chemistry and associated benefits.

3.1. Biodiesel production

Among the biofuels, the application of MWs or US in biodiesel synthesis or oil extraction and transesterification processes is fairly recent. Conversion of various types of oils (corn, coconut, rice bran, vegetable, rapeseed, sunflower, soybean, cottonseed, safflower, canola, camelina, used or waste vegetable oils, macauba, karanja, *jatropha curcas*, castor bean, castor, palm, yellow horn, animal fats, maize) to biodiesel via esterification and transesterification reactions was evaluated by many researchers [5,14]. Similarly, US enhanced extraction, esterification and transesterification reactions of various types of oils (coconut, olive, soybean, palm fatty acid distillate, *jatropha curcas*, *nagchampa*, rapeseed, sunflower, and waste cooking oils) were also widely studied [17].

The first combined MW–US reactor was introduced by Chemat et al. in 1996 [23]. In this study, MW and US enhanced reactions for pyrolysis of urea and esterification of propanol with acetic acid were evaluated. Conventional MW only and combined MW/US heating mechanisms were evaluated. The yields for urea pyrolysis were 45%, 46% and 57% for a reaction period of 1 hr. for conventional, MW only and combined MW/US heating mechanisms, respectively, while the yields for esterification reaction in 1 hr. reaction time were 80%, 91%, and 99% for the three mechanisms respectively. Later, this group also studied determination of copper in olive oil at a multi-gram scale and ambient conditions [24]. Further, the application of this hybrid technology in food and total Kjeldahl nitrogen analysis was also reported [25]. Cravotto et al. [26] first investigated the effect of MW and US irradiations either simultaneously or individually on extraction of oils from soybean germ and a marine microalga species. Their study reported a reduction in reaction times by up to ten-fold and an increase in oil extraction yields between 50% and 500%. This means higher yields (up to ten-fold can be obtained in a reaction time shortened by 10 times using MW and US irradiations. Comparison of individual and sequential applications of MWs and US in biodiesel synthesis has been studied recently. Many studies reported shorter reaction times, higher yields for MW process intensification while reduced solvent volumes and catalyst amounts were reported for US mediated reactions. MWs and US together have reduced the process reaction time as well as the amount of chemicals required significantly. MWs and US can be used simultaneously in a reaction environment in a single reactor or sequentially in separate reactors [14]. For example, biodiesel synthesis from a high acid value oil was studied using two-step esterification (to reduce the free fatty acid content that makes the oils suitable for transesterification reaction) followed by transesterification (chemical conversion of triglycerides into fatty acid methyl or ethyl esters) reactions [27].

As shown in Fig. 3, the solvent (alcohol donor) requirements were reduced for both esterification and transesterification reactions when MW or sequential MW and US methods were used (data taken from reference 27). For example, the oil to methanol molar ratios were 1:3 and 1:6 for esterification and transesterification reactions respectively for a conventional method but the same for the sequential MW and US mediated reactions were 1:2 and 1:4 respectively. In addition, the reaction times were significantly reduced from 20 and 90 minutes to 15 and 6 minutes. Reductions in these two parameters would also result in energy and cost reductions. As it is shown in Fig. 3, the total energy requirements for both reactions were about 10 times lower for MW and US method when compared with a conventional method. In our recent study, we reported on the effect of power density of the combined MW and US irradiations on transesterification of waste cooking oils [11]. Guldhe et al. studied the effects of MW and US separately on biodiesel production from algae (Scenedesmus sp.). Higher biodiesel conversion was reported for US (71%) effect when compared with MW (52%) effect [28].

MWs and US can be utilized not only in extraction and transesterification reactions of the biodiesel production but also in other process stages like feedstock pretreatment including harvesting and separation [14]. For example, as shown in Fig. 4, US can be used to gather (coagulation and flocculation of algal cells facilitated by the cell alignment to US field in a dilute algal

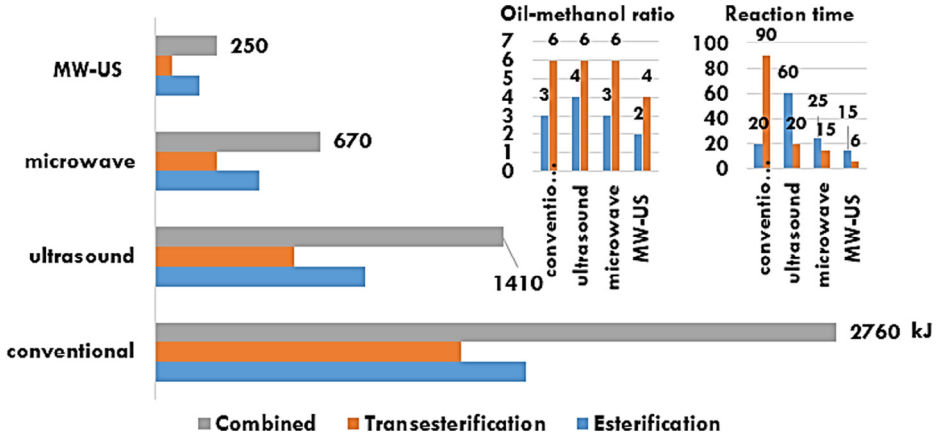

Fig. 3. Oil to methanol molar ratios (i.e., 1:3 or 1:6. . .etc), reaction time (min) and the energy requirements comparison for conventional, US, MW, and sequential MW and US based conversion of a non-edible (Nagchampa) oil to biodiesel via two-step esterification and transesterification reaction mechanism.

suspension as received from the cultivation stage, shown in Fig. 4a–c) the algal cells in the harvesting stage [29,30]. Once separated, concentrated algal suspension can be subjected to MW or MW–US irradiations to force-release the cell contents (mainly lipids) from the biological cell matrix and convert them simultaneously into biocrude for further treatment (Fig. 4d–f). Supercritical high temperature and high pressure reactions under MW irradiations are also possible to promote green extraction of lipids and other valuable bioproducts such as proteins [31]. In this process, water can be used as a green solvent eliminating toxic releases to the environment.

3.2. Bioethanol production

Three major feedstock categories for bioethanol production are: (i) sucrose-containing feedstock (e.g., sugar cane, sugar beet, sweet sorghum, and fruits), (ii) starch-containing feedstock (e.g., corn, milo, wheat, rice, potatoes, cassava and barley), and (iii) lignocellulosic biomass (e.g. wood, straw, grass, wasted crops and crop residues) [32]. Starch and sugar based feedstock have proven to be unsustainable due to unfavorable economics and other human interests leaving lignocellulosic and waste crops and wood residues as attractive feedstock. A variety of valuable products can be recovered from sugars and starch feedstock. These include ethanol, butanol, acetone, lactic acid, and amino acids, but lignocellulosic material is not simple to process. Similar to biodiesel production, bioethanol production from these lignocellulosic and other waste crop feedstock involves three essential steps [33,34]: (i) pretreatment of the feedstock; (ii) conversion of cellulose and hemicellulose into fermentable sugars; and (iii) fermentation of sugars into crude biofuels. The pretreatment step is a major hurdle which is required to improve the enzymatic hydrolysis of cellulose by reducing the effect of degree of polymerization, crystallinity of the cellulose, available surface area, lignin content, and moisture content. Complete utilization of available

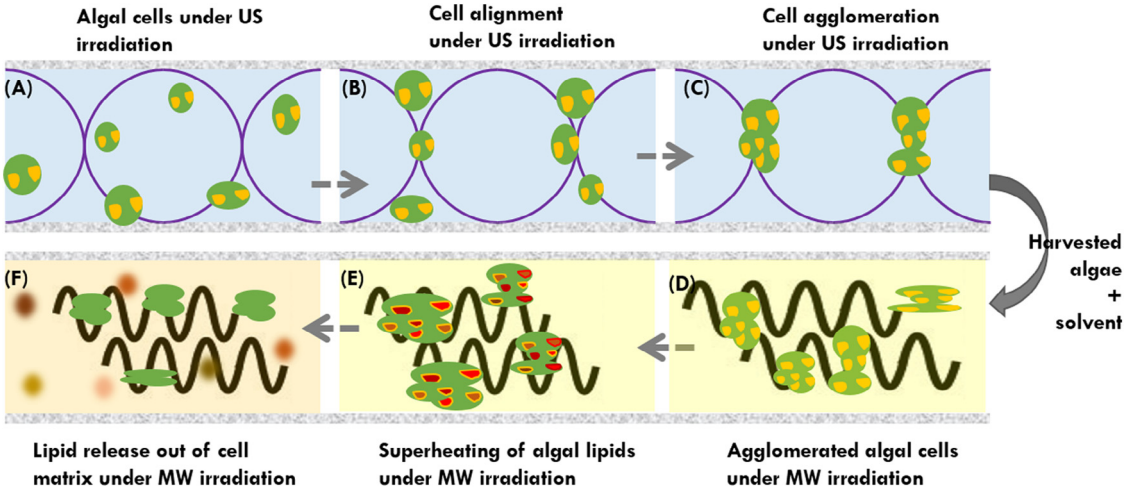

Fig. 4. Possible extraction and transesterification mechanisms for ultrasonic and MW induced reactors in series: (a) microalgal cells in water are exposed to ultrasonication; (b) ultrasonics align the algal cells along the vibrations; (c) ultrasonics coagulate to form floc and concentrate the algal cells; (d) concentrated algal cells exposed to MWs in the solvent medium; (e) MWs induce diffusive and disruptive mechanisms and create hotspots to extract the oils and lipids; (f) algal lipids extracted and transesterified by the MWs.

sugars in the biomass is the goal in bioethanol production [33]. Process intensification effects such as MWs and US could be useful in enhancing the effectiveness of the pretreatment methods [35]. MWs and US have a long history in the degradation of polysaccharides, water soluble carbohydrates and limited work on starch. US was first investigated on degradation of polysaccharides in 1933 by Flosdorf and Chambers [36]. Sonication improves hydrolysis of lignocellulosic materials into sugars and their subsequent fermentation to bioethanol. Degradation of starch from corn meal, maize and potato and other sources was also improved by US treatment. The effect of US (at both low and high frequencies) on carbohydrates in sulfuric acid were evaluated in many studies [37–40]. The application of MWs in starch depolymerization was reported in 1979 by Khan et al., in water, dilute hydrochloric acid and with chloride-based catalyst to enhance hydrolysis [41–43]. Many studies investigated the effect of MW or US pretreatment of corn meal, maize sugar, cellulose, switchgrass, rice hull, microcrystalline cellulose, cassava chip, kenaf core fiber, bamboo, waxy rice starch, maize starch, sugarcane, glucose and sugarcane bagasse [17]. Bioethanol yields from corn meal pretreated by MW or US were higher than conventional pretreatment. In a simultaneous saccharification and fermentation process, the yields increased by 6.82% and 8.48% for US and MW pretreatments respectively. The glucose utilization was also increased. US and MW pretreatments increased the maximum ethanol concentration produced in the SSF process by 11.15% and 13.40% (compared to the control sample), respectively [35].

Simultaneous or sequential use of MWs and US has not been explored much in bioethanol production. However, combined use of MWs and US in the catalytic conversion of starch-based industrial waste (wet potato sludge) into reducing sugars was evaluated recently [44]. Two hours of exposure to the combined MW and US irradiations at 60 °C in sulfuric acid converted 46% of the wet potato sludge to sugars. No significant conversion was observed when US alone was applied. About 35% of the waste was converted to sugars when MWs were used alone. For the combined irradiations, dry potato sludge and potato starch yielded 57% and 79% sugars whereas MW alone produced yields of 87% and 81% respectively. MWs and US can be used in other process related applications such as preparation of novel catalysts, surface modification of heterogeneous catalysts, and development of ionic liquids for biorefinery applications [45–51]. Application of these new materials might bring the benefits of efficient chemical and energy utilization, reduced waste products and alleviation of process reaction conditions.

3.3. Biogas production

Digestion of sludge and biomass requires optimum reaction conditions promoted by thermal energy and affected by other important process conditions such as pH, alkalinity, metal concentrations, and presence of micro-pollutants [52]. US and MWs can be conveniently used to heat the sludge and then destroy the cell walls to force out the cell components. An alternative would be to apply the US to weaken the cell walls and then subject the cell components to MW heating for digestion. Ideally, the two irradiations can be applied simultaneously to increase sludge digestibility. Biogas production remains the most technologically feasible and economically viable process for a variety of sludge and wastewater sources. However, limitations of energy recovery makes the process cost-inefficient. Application of MWs and US as process intensification effects may improve the biogas yields and in return the energy recovery and the overall process economics.

Apart from heating applications, non-thermal effects associated with MWs align the macromolecules possessing polarization with the electromagnetic field to cause possible breakage of hydrogen bonds [53]. This may result in enhanced sludge disintegration and hydrolysis which in turn increases the rate of anaerobic digestion, improves dewaterability, and inactivates fecal coliforms to produce Class A sludge. In high and low temperature (above and below boiling points) MW heating with both batch and continuous flow conditions, the biogas yield and dewaterability were increased by up to 30% and 40% respectively. US was also used frequently to disrupt the cellular matter, although mostly at laboratory scales. Disruption of cellular matter solubilizes the organic matter better and produces higher biogas.

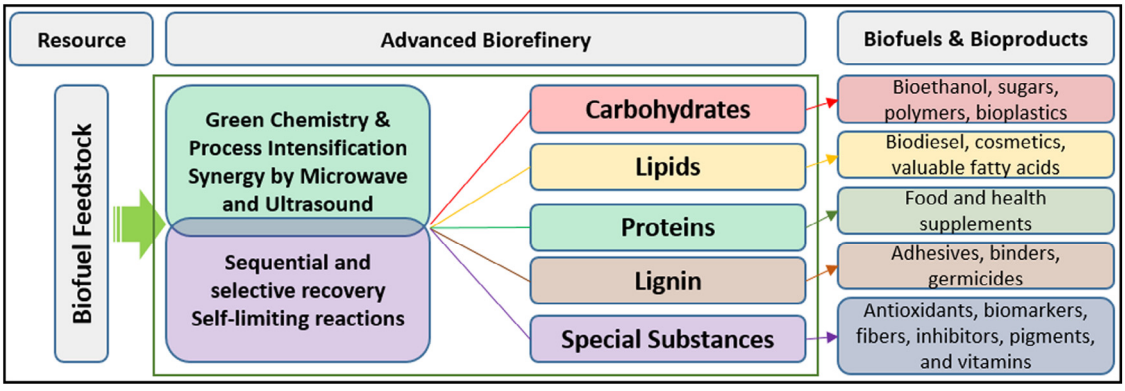

Fig. 5. An advanced MW/US enhanced biorefinery concept for sequential or selective recovery of various compounds suitable for synthesis of biofuels and bioproducts.

In addition to these energy carriers, MW and US irradiations can be utilized for selective recovery of carbohydrates, lipids, proteins, lignin, and special substances to produce a variety of high value bioproducts (see Fig. 5). MWs can be utilized for selective heating that promotes self-limiting reactions which in turn may enhance the selective recovery of valuable bioproducts. For example, proteins can be extracted from algal biomass prior to extracting lipids for biodiesel production. As an alternative, the lipid rich algal residue can be processed to produce bioethanol or biogas using thermochemical or biochemical processes.

4. Current issues with the hybrid technology and future prospects

The prospects for synergistic effect of MW and US enhanced process intensification based on the green chemistry principles are tremendous in any organic or inorganic synthesis or process as shown in Fig. 6. These two novel process intensification techniques have the potential to transform the current chemical synthesis and induce a paradigm shift. However, the costs (both capital and operational) of the process development seem to be an immediate concern. Apart from cost issues, other important factors influencing beneficial application of this hybrid technology are discussed next.

4.1. Understanding the biofuel chemistry – green chemistry is the path forward

It is paramount to understand and evaluate the process chemistry prior to determining the use of the MW/US technology. Different chemicals and solvents and materials interact with MWs and US in different ways. Some materials absorb MWs either completely or partially, and some reflect and some transmit (let MWs pass through). Similarly for US, the effect could be intense in some chemical synthesis and in some, it could be negligible. MW enhanced extraction using high dielectric solvents can be performed in closed vessels under high pressures [54]. Since these solvents are heated rapidly by the MWs, the temperature differential available in the reaction medium will drive the mass transfer between extractants and the feedstock. This process can be used for production of materials that are not sensitive to high temperatures. However, in the case of biodiesel production, high temperatures may not be favorable due to degradation of the valuable products such as algal biomass. A low dielectric constant possessing solvent can be used to extract the lipids. An example of low dielectric constant solvent is hexane. In a simultaneous extraction and transesterification reaction, addition of hexane helps increase the reaction time to expand the exposure of MWs to the reaction mixture. Hexane is an excellent solvent but has very low MW absorption properties. Hexane can be used as a temperature controlling agent while at the same time increasing heat and mass transfer in the extraction and transesterification reactions [55]. Another example is ethanol. It is a good solvent and reactant but its role in biodiesel synthesis is quite different from methanol. Ethanol also has good miscibility into organic solvents when compared with methanol which may increase the mass transfer properties especially under US irradiation [56].

The synergism of MWs and US has to be properly identified. This requires a mechanistic approach to elucidate the individual effects on the desired reaction. MW/US synergism may not be beneficial in all biofuel production processes. Either MW or US could be adequate for simple reactions (such as transesterification reaction). This needs to be verified to avoid misuse of resources. For example, in our recent study, we reported that US irradiation produced the highest biodiesel yield when compared with MWs and combined MW and US effect in a transesterification reaction [11].

4.2. Improving the energy efficiency in the MW/US hybrid reactors

Energy efficiency refers to the utilization of energy in the reaction and the conversion efficiency of the electrical energy into MW or US energy. The knowledge gap in efficient utilization of energy released through the two process intensification techniques must be addressed. The power density (W/m^3) and energy intensity (W/m^2) have to be analyzed for efficient utilization of energy [11,14,16]. These two process related actors will aid in process reactor design and product optimization. Power density which depends on the volume of the reaction mixture, expressed in small scales as W/mL, gives an estimate of the optimum energy required for the desired biofuel chemistry while the term energy intensity provides the basis for efficient design of the reactor to induce required energy intensity. The dimensions such as diameter and length of a reactor can be determined based on the optimum energy intensity

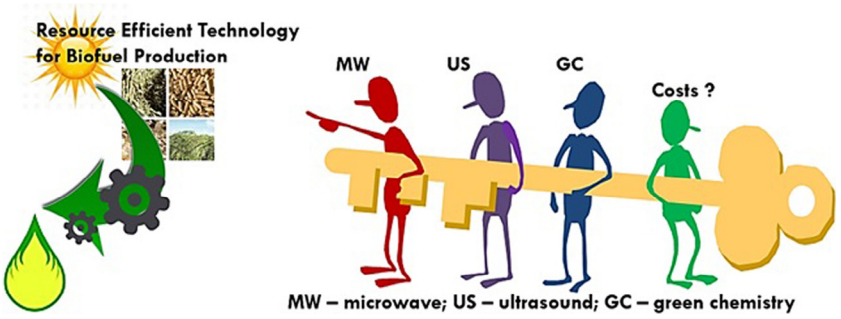

Fig. 6. MW and US synergism based on green chemistry principles as a pathway to resource efficient technology development for biofuel production.

which would also provide ideal power density for the reaction. Simultaneous or sequential application and the order of sequential application of the two process intensification effects should also be studied through well-designed experimental plan and analytical procedures. Standardization of the experimental results is important considering the present limitations in the literature. The energy density, reaction temperature and frequency (MW or US) and amplitude (US) and other pertinent information should be reported along with reactor specifications for all the studies. This ensures unbiased representation and evaluation of the data.

4.3. Increasing the recovery of valuable products

Current issues with the MW or US based methods is the cost intensive nature of the processes. Potential features that make these processes attractive are the high (cost) value of the product, significant advantage in the processing over conventional processing, limited plant space, and low cost electricity. In biofuel production, some of these requirements cannot be met. For example, the desired product (biofuel) costs are not favorable for implementation of these processes. For this reason, if selective recovery of valuable products from the biomass can be enhanced by manipulating the unique characteristics of these two process intensification effects, such process can be justified from all chemical, energy and cost related aspects.

The capital cost requirements for US, MW and sequential mode of operations were reported recently [27]. The capital cost requirements were reported to be 17.8%, 10%, and 7.5% higher when compared to the conventional method for sequential approach, MW and US respectively. This study also reported that despite the fact that capital cost requirement is marginally increased for the sequential mode of operation, there will be considerable savings in terms of methanol requirement (34%) and utility (2% preheating of oil) and processing times. The novel sequential operation approach presented in this work can significantly reduce the operating cost requirement for biodiesel synthesis, giving overall favorable economics. In addition, MW mediated pyrolysis for biomass conversion for rural and farm communities has been shown to be economically affordable [57].

4.4. Improving reactor design

Reducing the cost of construction for the hybrid reactors and improving the reactor design for energy efficiency may make this process intensification more relevant to biorefineries. For example, a synergistic effect can be produced in small reactor systems such as plug-flow reactors to promote gradient-less mixing which may lead to improved reaction rates and lower energy consumption. In large batch reactors, ultrasonics may not be able to induce the chemical/physical effects into the entire reactor contents, which depend on the reaction contents and their properties. The same applies to the MW irradiation [14]. US frequencies between 20 and 40 kHz have been reported to be suitable for extraction and chemical conversion (e.g., esterification and transesterification reactions) of biofuel feedstock [58,59]. About 20–25 kHz frequency is frequently reported in these applications. As an example, an ultrasonic frequency of 40 kHz favored maximum delignification while a frequency of 995 kHz was suitable for carbohydrate solubilization [60]. Higher frequencies can be used in other applications such as algal cell cultivation, harvesting and other applications. The ability of MWs to penetrate through materials also limits its applications. For large-scale design, two essential strategies can be considered. For simple chemical conversions such as a transesterification reaction involving oils, solvents and catalysts, MW irradiation frequency of 2450 MHz is adequate with ultrasonic horns in a plug-flow type or contact-type reactor design. For oil extraction and transesterification reactions (such as direct extraction and transesterification of algal lipids), the frequency of the MWs and US may need to be altered [5,16]. MWs at 915 MHz (used industrially) have much higher penetration depths into the material when compared to the higher frequency of 2450 MHz commonly used in laboratory-sized equipment. The higher penetration depths allow for much larger diameter tubes and processing flow rates. MW generators can be built for significantly higher power efficiencies when compared to smaller generators. For US, longitudinally vibrating horns can be beneficial for continuous processing [11]. Control of MW–ultrasonic reactions is also subject to similar limitations as any thermal process; however, their intensity and energy supply can be controlled easily to achieve desired reactions [61].

5. Concluding remarks

Superior benefits associated with MWs and US as process intensification effects come with greater challenges and limitations. These limitations provide opportunities for further research in the near future. Heat and mass transfer limitations have been addressed in the hybrid systems but the power control needs to be improved. One major hurdle that needs to be overcome at present is to make this hybrid system economically viable. The application of longitudinal US application together with MWs in continuous plug-flow type reactor design must be developed for efficient utilization of these two process intensification methods. Exploiting the unique characteristics inherent to MWs and US such as rapid and selective heating and self-limiting reactions, heat and mass transport and energy dissipation for selective and sequential recovery of multiple high value added bioproducts proves to be an important endeavor to address the cost issues associated with this hybrid technology considering the present biorefinery economics.

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Conflict of interest

No conflicts of interest.

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