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NOVEL EXPERIMENTAL STUDIES FOR BIODIESEL PRODUCTION USING PROCESS INTENSIFICATION TECHNIQUES DEVELOPED AT A HIGHER EDUCATION INSTITUTE OF INDIA

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ABSTRACT: Globally fast depleting fossilized fuel reserves and increasing environmental pollution problems are the key motivating factors to pursue research on alternative fuels derived from biomass, which can fulfil the increasing future energy demand for sustainable development. In this regard, biodiesel as a sustainable alternative helps to protect the environment due to its non-toxic, renewable, and biodegradable nature and produces less sulphur emissions and greenhouse gases. It is easy to use as well as clean and safe to handle as compared to gasoline diesel. Biodiesel research has remained in the high priority areas for researchers around the globe for the last two decades due to the number of challenges such as to make it an economic and industrially viable product.

Introduction

Globally fast depleting fossilized fuel reserves and increasing environmental pollution problems are the key motivating factors to pursue research on alternative fuels derived from biomass, which can fulfill the increasing future energy demand for sustainable development. In this regard, biodiesel as a sustainable alternative helps to protect the environment due to its non-toxic, renewable, and biodegradable nature and produces less sulphur emissions and greenhouse gases. It is easy to use as well as clean and safe to handle as compared to gasoline diesel. Biodiesel research has remained in the high priority areas for researchers around the globe for the last two decades due to the number of challenges such as to make it an economic and industrially viable product.

The use of process intensification techniques along with in-situ concept in biodiesel production has the potential to reduce both energy requirement and cost involved at different stages of biodiesel production process. Moreover, there is a lot of research scope for optimizing the properties of the biodiesel and its blends (binary as well as ternary) so that the desired compression ignition engine performance and combustion characteristics can be achieved with a focus on the emission reduction.

The prime objectives of present experimental research work is on design and development of an environment-friendly, energy-effective and industrially viable process intensification (PI)- techniques {Ultrasound, Microwave, and Conjoint (microwave + ultrasound) technique} using both homogeneous (potassium hydroxide, KOH) and heterogeneous (calcium oxide, CaO) catalysts to synthesize biodiesel from various combinations of waste cooking oil (WCO), blended oils and seeds (normal and irradiated) as a feedstock.

In Microwave irradiation, microwave energy acts as a non-ionizing radiation energy source caused due to molecular motions of ions and rotation of the dipoles. It does not disturb the molecular structure but not able to remove the limitation of mass transfer. Whereas, ultrasound has a significant formation of microbubbles that affect the rate of various processes but is not enough to cause an overall escalation in temperature of the reaction mixture. The ultrasound and microwave techniques, independently have definite limitations like weakening effect and low diffusion depth respectively. This necessitates to develop and embrace a suitable conjoint microwave and ultrasound effect. Thus, the combination of both irradiations (refer Fig. 1) acting perpendicular to each other, creates the physical effect which includes the formation and breakdown of microbubbles that causes the formation of high pressure and heat release cycles at micro-scale resulting in improved mass and heat transfer. Thus, the high energy level of bubble cavitation under ultrasound can prompt particle fragmentation and molecule excitation, whereas microwave polarization can encourage dielectric volumetric heating and selective heating of molecules. The summary of the various experimental studies performed at CBBS (Centre for Biofuel and Bioenergy Studies), PDEU are given below:

The experimental results of the study performed on ultrasound process [1,2] showed the enhanced biodiesel yield (98% for KOH and 96.45% for CaO catalyzed conditions) from WCO and significant reduction in the reaction period (10 min), making the process energy-efficient in comparison to the conventional mechanical stirring (MS) technique which is commonly used by the biodiesel industry. The optimization study of process parameters was performed using a Box-Behnken design of experiments method.

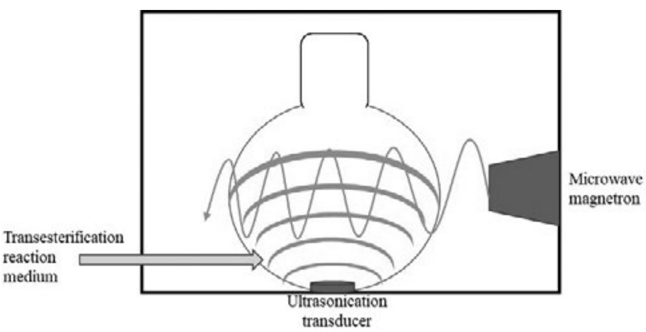

FIGURE 1: Conceptual diagram of wave propagation of microwave and ultrasound

Similarly, experimental study on microwave-assisted biodiesel production technique [1,3] from WCO has shown significant results in terms of lower reaction time (9.7 min), with higher yield (96.77% for KOH and 90.5% for CaO catalyzed conditions) and achieved high energy efficiency. In this process, the optimization of process parameters was done using the full factorial design of experiments.

The scarcity of feedstock is the major concern for biodiesel production, and this can be resolved by blending the available non-edible feedstock. This approach will provide option to prepare a low-cost feedstock with large availability and uniform properties. Further it has been observed that blending of feedstock improves the biodiesel properties. The conjoint microwave + ultrasound technique was used for biodiesel production using the blends of WCO and raw castor oil (RCO). For the first time, blending ratio as a unique process parameter for combination of oils was considered for biodiesel production process. The optimization of process parameters was performed via the Box-Behnken design of experiments. The study showed that the conjoint effect of the microwave + ultrasound technique produces biodiesel with improved fuel properties. Also, higher biodiesel yield (93.38% for KOH and 92.19% for CaO catalyzed conditions), lower reaction time (10 min), and energy requirements makes it a superior energy-efficient process in comparison to that of individual microwave and ultrasound subsystem as well as the MS technique [4,5]. First time the “blend ratio” as a unique parameter is optimized for blended oil transesterification and 60RCO40WCO fraction was found to be the optimum one to produce biodiesel yield of 93.38% for KOH catalyzed condition and 92.19% biodiesel yield for CaO catalyzed conditions.

The reaction kinetic analysis was performed for all three PI reactor systems assuming pseudo-first-order kinetic. The activation energies for PI techniques were observed to be reduced significantly (ultrasound reduces the activation energy by 1.7 and 1.5 times in comparison to MS for KOH and CaO conditions respectively, reduction in activation energy using the microwave reduces the activation energy by 2.6 and 1.7 times in comparison to MS for KOH and CaO conditions respectively, and for conjoint technique the activation energy was reduced by 2.5 and 1.8 times for KOH and CaO catalyzed conditions respectively) in comparison to MS technique. Further, energy analyses were performed for all the above-mentioned processes. Parameters like dissipated power, delivered power, and percentage efficiency were estimated and analyzed. These analyses effectively demonstrated that the PI techniques are energy-efficient (11 times for ultrasound, 21 times for microwave and 3 times for conjoint technique) in comparison to MS technique. Based on the batch size process optimization results, commercialization potentiality of all the three techniques was examined by performing a scale-up study. A ten-fold scale up of 50 mL batch size was taken to perform the experiments based on the optimized parameters and it showed that about 90% biodiesel yield was obtained within a short span of 15 - 20 min. Using recently developed large scale ultrasound and microwave equipment available in the market, the successful commercialization of PI techniques can be achieved. All the processes have shown bright prospects for commercialization for small scale applications with certain modifications (based on type of equipment) in process equipment and design parameters. The physicochemical properties of produced biodiesel were correlated with ASTM petrodiesel standard and biodiesel fuel standards. All the fuel properties found to comply within ASTM biodiesel standard limits and at par with the petrodiesel.

Biodiesel is produced through transesterification reaction that is conventionally carried out using mechanical stirring post oil extraction that makes it a two-step process. In continuation to the above mentioned experimental research, the present study demonstrates innovative single step in-situ biodiesel production process eliminating oil extraction stage using coordinated ultrasound-microwave reactor. Castor is a non-edible oil crop due to presence of toxic element ricien in its chemical structure. Castor oil has unsaturated ricinoleic acid in higher proportion (85-90%) which has hydroxyl bond in its chemical structure causing high viscosity. The radiation chemistry is known to cause the changes in the chemical structure of the oil and can help to control its properties. The effect of gamma rays irradiation on castor seeds and optimum conditions of insitu transesterification reaction parameters for biodiesel production are investigated thoroughly. Normal as well as gamma irradiated castor oil seeds have been used for the in-situ biodiesel production using simultaneous intensification by ultrasound and microwave (hybrid intensification, refer Fig. 2). Gamma irradiation found to affect the fatty acid profile of the oil obtained from the castor seeds. The proportion of ricinoleic fatty acid is found to be decreased in fatty acid profile of gamma irradiated castor seeds compared to normal castor seeds. Formation of squalene was detected and its proportion was found to be increased up to 2.07% in castor seeds irradiated with dosage value of 9 kGy. The viscosity of castor oil obtained through gamma irradiated castor seeds was decreased to 195 cst (for 9 kGy) as compared to 210 cst of castor oil obtained through normal castor seeds.

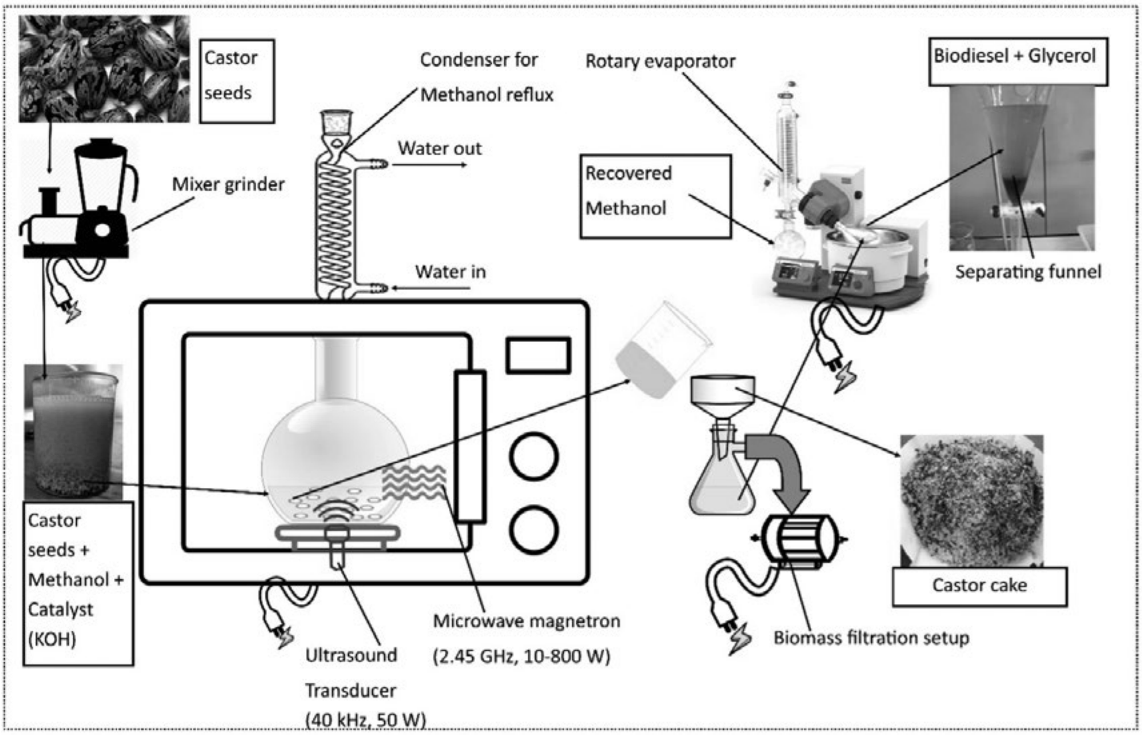

FIGURE 2: Schematic of lab scale in-situ transesterification of castor seeds using hybrid reactor

For normal seeds the maximum biodiesel yield of 93.5 ± 0.76 percent is achieved for optimum reaction conditions of 350:1 methanol to oil molar ratio, 1.71% catalyst amount, 44 °C reaction temperature, and 30 min of reaction time using response surface methodology (RSM) coupled with central composite design (CCD) [6]. The optimum reaction conditions for gamma irradiated castor seeds are obtained using RSM coupled with Box-Behnken Design (BBD) which includes: gamma radiation dosage 9 kGy, methanol to oil molar ratio of 288:1 (6.5 ml of methanol per gram of castor seeds; v/w), catalyst amount 1.33%, 52.5°C reaction temperature and 30 min reaction time. The biodiesel yield obtained from gamma radiated castor seeds by applying these optimized reaction conditions is 96.04 ± 0.53 % which is 2.5% higher as compared to the biodiesel yield obtained from non-irradiated castor seeds. The methanol to oil molar ratio is found to be reduced by 17.71% while catalyst loading requirement is reduced by 22.22% which makes the process environmentally as well as economically viable. It is found that reaction rate of the transesterification has been improved by 30-40% and activation energy has been decreased by 50% (14 kJ/mol) when compared to transesterification reaction of non-irradiated castor seeds (28.27 kJ/mol). The gamma irradiation causes formation of squalene (0.40 to 2.07%) which is not observed in the original oil compositions of non-irradiated castor seeds. Physico-chemical properties of biodiesel were compared with biodiesel standards (ASTM D6751 and EN 14214) and found satisfactory for both the cases. The calorific value of the biodiesel obtained through gamma radiated castor seeds (39.05 ± 0.2 MJ/kg) is improved by 2.7% compared to biodiesel obtained through normal castor seeds (38.01 ± 0.2 MJ/kg). The pour point is comparable and is found to be as low as -35°C. The oxidation stability of the biodiesel produced from the gamma radiated castor seeds is higher and has been found to be unaffected upon irradiation.

In the above mentioned experimental research, first time conjoint microwave + ultrasound reactor has been applied for biodiesel production from transesterification of blended RCO and WCO oil mixture as well as insitu combination. It can be concluded that the blending of inexpensive non-edible oil/ waste cooking oil has been proven to be a promising solution for the production of biodiesel. This is because (a) the final product cost will reduce, (b) dependency of edible oil will be less and (c) different types of non-edible/ waste oils can be blended in different proportions based on the availability. The conjoint effect of process intensification techniques (microwave + ultrasound) results in a synergistic effect of mass transfer and heat transfer that enhances the biodiesel yield within a short reaction time. It also tends to improve the physicochemical properties of biodiesel. Thus, the present work demonstrated a successful comprehensive experimental study to assess the overall performance of PI techniques in reference to the MS process.

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