

Enhancement of Biodiesel Production via Ultrasound Technology: A Mathematical Study

Xianbing Cao, Sk Mosaraf Ahammed, Siddhartha Datta, Jahangir Chowdhury, and Priti Kumar Roy*

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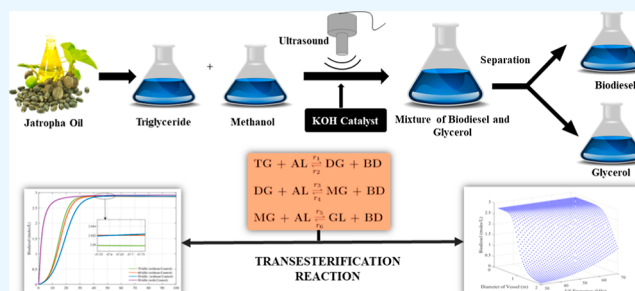
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ABSTRACT: Biodiesel is one of the alternative renewable energy sources that has received a lot of attention since it is clean, green energy. Different sources can be used for the production of biodiesel, but the most appropriate and economical method relies on the transesterification of methanol with the nonedible vegetable oil from the fruit of the *Jatropha curcas* plant. Molar ratio, vessel diameter, catalyst concentration, and ultrasound all have a substantial influence on the synthesis of biodiesel by the transesterification process. Among these factors, the diameter of the vessel and the ultrasonic effect through mass transfer limitations have a significant impact on successful reaction completion. In this research work, we have developed a mathematical model to analyze the three-step transesterification process and side saponification reaction in the presence of a potassium hydroxide catalyst. The model considers the influence of mixing intensity variations, including ultrasound, on the mass transfer in different phases. The mass transfer rate is calculated using the modified Dittus–Boelter correlation. An optimal control approach through the minimum principle by Pontryagin is applied to maximize the production of biodiesel at minimal cost. The novelty of this research, which we have derived from our analytical as well as numerical results, considering industrial processes, is that more than 97% biodiesel yield conversion is to be obtained at 50 kHz ultrasound frequency, a 6:1 methanol-to-*Jatropha*-oil molar ratio, and 1 m of vessel diameter within 50 min using optimal control theory.



1. INTRODUCTION

Presently, fossil fuels are the primary source, meeting more than 90% of the world's energy requirements. Excessive fossil fuel consumption has a direct impact on the environment, causing global warming and the release of greenhouse gases.¹ To prevent this, research into ecofriendly alternative fuels has become incredibly important in the industry. Among various renewable sources, biodiesel is considered to be the most favorable alternative. Biodiesel can be produced from a variety of edible and nonedible vegetable plant-based oils, animal fats, and waste cooking oils. Currently, over 95% of biodiesel synthesis relies on edible oil sources, resulting in higher production costs and a worsening of food scarcity.² So it is crucial to examine suitable feedstock for producing economically viable biodiesel. As a nonagricultural, nonedible, affordable, and sustainable feedstock, *Jatropha curcas* Linnaeus is regarded as the most advantageous alternative.³ *Jatropha curcas* belongs to the Euphorbiaceae family and can thrive in marginal lands across regions with varying rainfall, such as Central and South America, Southeast Asia (particularly India and Indonesia), Africa, and various other parts of the globe. *Jatropha* seed contains 35–40% oil, and the kernel of *Jatropha curcas* contains 50–60% oil.⁴ This oil serves as feedstock for biodiesel synthesis. In the realm of commercial biodiesel production from vegetable oils or fats, the

most prevalent approach is the base-catalyzed transesterification reaction, which occurs between vegetable oil or fat and alcohol while a catalyst is present.^{5,6} Biodiesel production through transesterification is shown in Figure 1. The transesterification reaction of vegetable oil and alcohol is a three-step reversible reaction in which 1 mol of triglyceride reacts with 3 mol of alcohol, producing 3 mol of biodiesel and 1 mol of glycerol as a byproduct. Researchers such as Bambase et al.,⁷ Stamenković et al.,⁸ De Paola et al.,⁹ Diwekar and Benavides,¹⁰ Roy et al.,¹¹ and Chowdhury et al.¹² have provided evidence that the successful production of biodiesel depends on various reaction parameters, including temperature, molar ratio of alcohol-to-oil, mixing effects, and catalyst concentration.

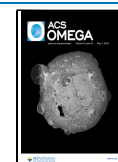
Usually, alcohols are polar and oils are nonpolar; as a result, alcohol and oil are nearly immiscible, and the mass transfer resistance is very high between them.¹³ Commercially,

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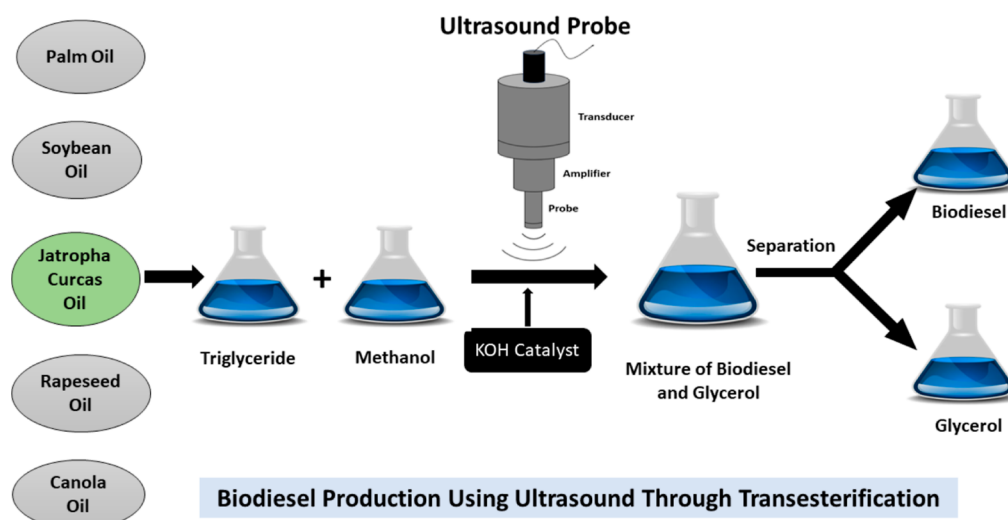


Figure 1. Process of biodiesel production through transesterification of various vegetable oils.

mechanical stirring is employed to decrease mass transfer resistance in the biodiesel production process through the batch reactor.¹¹ Ultrasound intensity is another technique that reduces mass transfer resistance between oil and alcohol.^{14–16} The use of ultrasound in biodiesel manufacturing offers the following benefits: (i) a shorter processing duration, (ii) less amount of alcohol and catalyst requirements, (iii) lower reaction temperatures, and (iv) shorter separation time of biodiesel and glycerol.¹⁷ In fact, ultrasound produces a higher chemical yield than conventional mechanical stirring.¹⁸ Ultrasound has been used successfully to increase the rates of mass transfer and reaction rates in a variety of homogeneous^{19,20} and heterogeneous^{21,22} systems. According to Stavarache et al.,²³ high-frequency ultrasound (40 kHz) speeds up the transesterification process and increases biodiesel yield. Colucci²⁴ demonstrated that the application of ultrasonication improved the apparent rate constants of alkaline transesterification in his experiments. By using a homogeneous catalyst and several heterogeneous catalysts, Georgogianni et al.^{15,25} showed that using ultrasound considerably boosted the transesterification reaction of soybean frying oil in comparison to mechanical stirring. Lifka and Ondruschka¹⁴ showed that a conversion of 87% was obtained to a molar ratio of 6:1 and 0.5–1% sodium hydroxide in 30 min by using ultrasound (24 kHz; 200 W). Santos et al.²⁶ produced a 98.2% biodiesel yield in 90 min from fish (Nile Tilapia) oil and methanol at 40 kHz ultrasound frequency, 9:1 methanol-to-oil molar ratio, and 2.0 wt % catalyst concentration. Numerous researchers have explored the impact of mass transfer limitations in biodiesel production through mechanical stirring;^{27,28} however, mathematical studies based on mass transfer due to ultrasound for biodiesel production from *Jatropha curcas* oil have not been explored yet.

In this research article, we adopt the identical reaction mechanism outlined in our prior publications,¹² considering the impact of ultrasound on the immiscible mixture and the mass transfer resistance between methanol and *Jatropha* oil for the production of biodiesel. This study investigates the impact of ultrasound on the immiscible mixture and the mass transfer resistance between methanol and *Jatropha* oil. We calculated the mass transfer rate using the modified Dittus–Boelter correlation with the variation of ultrasound frequencies and vessel diameters. The control theoretical approach to ultrasound

frequency has been investigated in order to achieve the maximum biodiesel yield by minimizing the mass transfer resistance. The system has been studied numerically and investigated the ultrasound-assisted biodiesel yield dependency on vessel size and the molar ratio of oil and methanol. Using control approach, we have obtained more than 97% biodiesel yield within 50 min at a 50 kHz ultrasound frequency with a 6:1 methanol-to-oil molar ratio when the vessel diameter is 1 m, which validates the industrial process.

2. FORMULATION OF MATHEMATICAL MODEL

In order to depict a basic mathematical model for the transesterification reaction of alcohol (methanol) and *Jatropha curcas* oil (triglyceride), we have relied on the following assumptions:

(a1) Biodiesel production through transesterification of *Jatropha* oil with methanol is a chemical process that involves three stepwise and reversible reactions.²⁹

(a2) The reaction mixture of methanol and oil includes a very little amount of water (0.2% w/w), so the hydrolysis reaction has been neglected.³⁰

(a3) Due to the presence of a small amount of free fatty acid (FFA, 1% w/w) in *Jatropha* oil, triglyceride, FFA, and the produced biodiesel will participate in the saponification reaction with a KOH catalyst.³¹

(a4) The mass transfer coefficient r_c due to ultrasound is given by

$$r_c = 0.023 \frac{D}{d} (Re)^{0.8} (Sc)^{0.33} \quad (1)$$

where $Re = \frac{d^2 \rho H}{\mu}$ and $Sc = \frac{\mu}{\rho D}$ are called the Reynolds number and Schmidt number, respectively.³² Here D , ρ , and μ are the mass diffusivity, density, and viscosity of *Jatropha* oil, respectively. H is the applied ultrasound frequency, and d is the diameter of the production vessel. The inverse of the mass transfer coefficient denotes the mass transfer resistance for the molecules to reach the reaction site, which depends not only on the creation of turbulence inside the vessel but also on the diameter of the vessel. That is why $\frac{r_c}{d}$ denotes the total mass transfer rate coefficient. In this case, the total mass transfer resistance depends on the sonicator frequency as well as the size

of the vessel. Thus, the total mass transfer rate constant (M_c) becomes

$$M_c = \frac{r_c}{d} = 0.023 \frac{D}{d^2} (Re)^{0.8} (Sc)^{0.33} = 0.023 \frac{D}{d^2} \left(\frac{d^2 \rho H}{\mu} \right)^{0.8} \left(\frac{\mu}{\rho D} \right)^{0.33} \quad (2)$$

Here, Figure 2 represents the log–log plot of M_c and Reynolds number Re using parameter values from Table 1. The figure

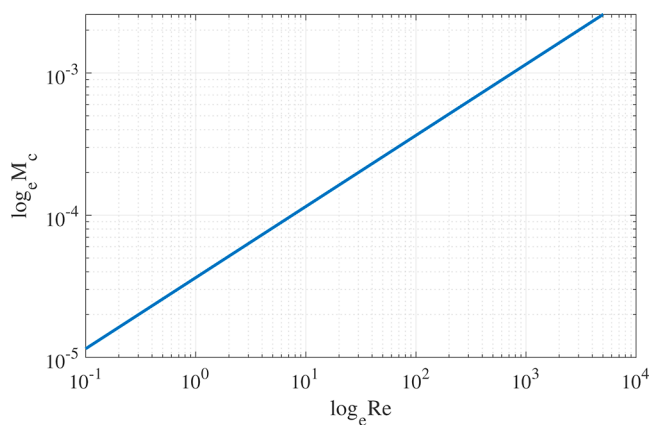


Figure 2. Correlation of mass transfer rate constant and Reynolds number.

Table 1. Some Liquid Properties of *Jatropha curcas* Oil and Input Range of Ultrasound and Vessel Size Used in the Reaction at 50 °C

parameter	Definition	Value
D	diffusivity of <i>Jatropha</i> oil	$5.49 \times 10^{-6} - 1.16 \times 10^{-5} \text{ m}^2 \text{ s}^{-133}$
ρ	density of <i>Jatropha</i> oil	$896.51 \text{ kg m}^{-334}$
μ	viscosity of <i>Jatropha</i> oil	$24.8646 \text{ kg m}^{-1} \text{ s}^{-134}$
d	diameter of the tube	1–2 m
H	ultrasound frequency	30–70 kHz

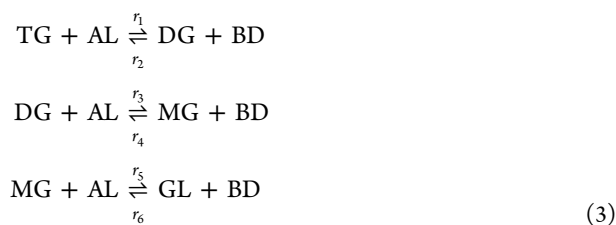
demonstrates how the mass transfer reaction constant increases as the Reynolds number increases. The creation of turbulence in the reaction system is enhanced with the increase of Reynolds number. Consequently, the mass transfer resistance, which is inversely proportional to the mass transfer coefficient between *Jatropha* oil and methanol, decreases, and the mass transfer reaction constant increases. Table 2 shows the values of the mass transfer coefficient found from the correlation defined above at various ultrasound frequencies and vessel diameters.

Table 2. Mass Transfer Coefficient (M_c) for Different Ultrasound Frequencies and Vessel Sizes at 50 °C Temperature

H (kHz)	D ($\text{m}^2 \text{ s}^{-1}$)	D (m)	P (kg m^{-3})	μ ($\text{kg m}^{-1} \text{ s}^{-1}$)	M_c (m s^{-1})
40	9.1×10^{-6}	1	896.51	24.8646	1.0×10^{-3}
50	9.1×10^{-6}	1	896.51	24.8646	1.2×10^{-3}
60	9.1×10^{-6}	1	896.51	24.8646	1.4×10^{-3}
70	9.1×10^{-6}	1	896.51	24.8646	1.6×10^{-3}
40	9.1×10^{-6}	2	896.51	24.8646	8.0×10^{-4}
50	9.1×10^{-6}	2	896.51	24.8646	9.0×10^{-4}
60	9.1×10^{-6}	2	896.51	24.8646	1.0×10^{-3}
70	9.1×10^{-6}	2	896.51	24.8646	1.2×10^{-3}

(a5) Though there is a slight temperature elevation when using ultrasound, we keep the temperature constant at 50 °C throughout our work as viscosity and density change with respect to temperature. Moreover, Chowdhury et al.¹² demonstrated that the saponification reaction accelerates and biodiesel conversion decreases when the temperature exceeds 50 °C.

(a6) The transesterification reaction for biodiesel synthesis occurs through three stepwise reversible reactions in the presence of a KOH catalyst.²⁹ In the first reversible step, 1 mol of triglyceride (TG) reacts with 1 mol of methanol (AL), yielding 1 mol of biodiesel (BD) and 1 mol of diglyceride (DG). During the second reversible step, 1 mol of diglyceride (DG) reacts with 1 mol of methanol (AL) to produce 1 mol each of biodiesel (BD) and monoglyceride (MG). In the final reversible step, 1 mol of monoglyceride (MG) reacts with another 1 mol of methanol (AL), resulting in 1 more mole of biodiesel (BD) and 1 mol of glycerol (GL) as the byproduct. In total, 1 mol of triglyceride reacts with 3 mol of methanol to produce 3 mol of biodiesel and 1 mol of glycerol. The stepwise reaction scheme is shown as



Also, there will be some soap formation of potassium by the side reaction of catalyst KOH with triglyceride, diglyceride, monoglyceride, biodiesel, and FFA. Due to the slow reaction rate, we have neglected soap formation from diglycerides and monoglycerides in our model.^{12,35} This saponification reaction will happen in three steps as shown below



where, r_1 , r_3 , and r_5 are the rate constants for the forward reaction, r_2 , r_4 , and r_6 are the rate constants for the backward reaction of the main reaction, and r_7 , r_8 , and r_9 are the rate constants for the forward reaction of the side saponification reaction. All these rate constants follow the Arrhenius equation by the relation $r_i = A_i e^{\frac{-E_{A_i}}{RT}}$,¹⁰ where A_i , T , R , and E_{A_i} are the frequency factor, the reaction temperature, the universal gas constant, and the activation energy, respectively, for each

Table 3. Values of Various Reaction Constants at 50 °C and Maximum Biodiesel That Can be Produced in an Ideal Situation

parameter	definition	value
r_1	forward reaction constant	0.0500 mole ⁻¹ L min ⁻¹
r_2	backward reaction constant	0.1099 mole ⁻¹ L min ⁻¹
r_3	forward reaction constant	0.1220 mole ⁻¹ L min ⁻¹
r_4	backward reaction constant	0.2147 mole ⁻¹ L min ⁻¹
r_5	forward reaction constant	0.2420 mole ⁻¹ L min ⁻¹
r_6	backward reaction constant	0.0070 mole ⁻¹ L min ⁻¹
r_7	forward reaction constant	0.00281 mole ⁻¹ L min ⁻¹
r_8	forward reaction constant	0.00279 mole ⁻¹ L min ⁻¹
r_9	forward reaction constant	0.2817 mole ⁻¹ L min ⁻¹
B_{\max}	maximum biodiesel production	3 moles L ⁻¹

component $i = 1, 2, \dots, 9$. The values of r_1 to r_9 obtained by using the values of A_i and others in¹⁰ with the help of Arrhenius equation are shown in Table 3.

Based on the above assumptions, the governing differential equations of the main reaction and side reaction scheme can be written as

$$\begin{aligned}
 \frac{dY_B}{dt} &= r_1 Y_T Y_A - r_2 Y_D Y_B + r_3 Y_D Y_A - r_4 Y_M Y_B + r_5 Y_M Y_A \\
 &\quad - r_6 Y_G Y_B - r_8 Y_B Y_K \\
 &\quad + M_c Y_B \left(1 - \frac{Y_B}{B_{\max}} \right) \\
 \frac{dY_T}{dt} &= -r_1 Y_T Y_A + r_2 Y_D Y_B - r_7 Y_T Y_K \\
 \frac{dY_D}{dt} &= r_1 Y_T Y_A - r_2 Y_D Y_B - r_3 Y_D Y_A + r_4 Y_M Y_B \\
 \frac{dY_M}{dt} &= r_3 Y_D Y_A - r_4 Y_M Y_B - r_5 Y_M Y_A + r_6 Y_G Y_A \\
 \frac{dY_A}{dt} &= -r_1 Y_T Y_A + r_2 Y_D Y_B - r_3 Y_D Y_A + r_4 Y_M Y_B \\
 &\quad - r_5 Y_M Y_A + r_6 Y_G Y_B + r_8 Y_B Y_K \\
 \frac{dY_G}{dt} &= r_5 Y_M Y_A - r_6 Y_G Y_B + r_7 Y_T Y_K \\
 \frac{dY_K}{dt} &= -\frac{dY_S}{dt} = -(r_7 Y_T Y_K + r_8 Y_B Y_K) \\
 \frac{dY_F}{dt} &= -\frac{dY_W}{dt} = -r_9 Y_F Y_K
 \end{aligned}
 \tag{5}$$

where Y_B , Y_T , Y_D , Y_M , Y_A , Y_G , Y_K , Y_S , Y_F , and Y_W are the concentrations of biodiesel, triglyceride, diglyceride, monoglyceride, methanol, glycerol, potassium hydroxide, soap, FFA and water, respectively, with the initial conditions $Y_B(0) = 0$, $Y_T(0) = Y_{T0}$, $Y_D(0) = 0$, $Y_M(0) = 0$, $Y_A(0) = Y_{A0}$, $Y_G(0) = 0$, $Y_K(0) = Y_{K0}$, $Y_S(0) = 0$, $Y_F(0) = Y_{F0}$, and $Y_W(0) = 0$. We have designed our model with a logistic approach, incorporating the term $M_c Y_B \left(1 - \frac{Y_B}{B_{\max}} \right)$ during its development. Here, Y_B denotes biodiesel concentration at any time t , and B_{\max} represents the maximum biodiesel production in the transesterification reaction. Both have the same unit, moles/L. This expression has been utilized in a logistical sense, since the total mass transfer rate goes up as mass transfer resistance diminishes, and after

reaching a specific ultrasound frequency and vessel diameter, the mass transfer resistance becomes insignificant.

3. OPTIMAL CONTROL PROBLEM FOR CHEMICAL REACTION SYSTEM

A subset of mathematical optimization, optimal control theory, is concerned with identifying the control parameters required to achieve laboratory-oriented experimental control over a dynamical or chemical system for a designated time frame, with the aim of optimizing an objective function. Here, we have applied optimal control of ultrasound frequency. In the beginning, the reaction is very slow due to the high mass transfer resistance between methanol and Jatropha oil. By applying ultrasound frequency, the initial mass transfer resistance is reduced. Once the reaction starts, it continues at a rapid pace, so there is no need for ultrasound frequency after some time for smooth progression of the reaction. Therefore, for cost-effectiveness, we turned off the ultrasound frequency in the reaction system.

In this section, theoretical selection of the range of ultrasound frequency is our primary goal to achieve the maximum amount of biodiesel. Also, our objective is to minimize the cost function. Let the ultrasonic frequency input at time t be represented by the control input variable z with $0 \leq z \leq 1$. Here, the value $z = 1$ denotes the highest utilization of ultrasound frequency, while $z = 0$ indicates the absence of frequency.

Mathematically, the control-induced system corresponding to the system (5) is formulated as

$$\begin{aligned}
F_1 &= \frac{dY_B}{dt} = r_1 Y_T Y_A - r_2 Y_D Y_B + r_3 Y_D Y_A - r_4 Y_M Y_B + r_5 Y_M Y_A \\
&\quad - r_6 Y_G Y_B - r_8 Y_B Y_K \\
&\quad + M_c Y_B \left(1 - \frac{Y_B}{B_{\max}} \right) z \\
F_2 &= \frac{dY_T}{dt} = -r_1 Y_T Y_A + r_2 Y_D Y_B - r_7 Y_T Y_K \\
F_3 &= \frac{dY_D}{dt} = r_1 Y_T Y_A - r_2 Y_D Y_B - r_3 Y_D Y_A \\
&\quad + r_4 Y_M Y_B \\
F_4 &= \frac{dY_M}{dt} = r_3 Y_D Y_A - r_4 Y_M Y_B - r_5 Y_M Y_A \\
&\quad + r_6 Y_G Y_B \\
F_5 &= \frac{dY_A}{dt} = -r_1 Y_T Y_A + r_2 Y_D Y_B - r_3 Y_D Y_A \\
&\quad + r_4 Y_M Y_B - r_5 Y_M Y_A + r_6 Y_G Y_B + r_8 Y_B Y_K \\
F_6 &= \frac{dY_G}{dt} = r_5 Y_M Y_A - r_6 Y_G Y_B + r_7 Y_T Y_K \\
F_7 &= \frac{dY_K}{dt} = -(r_7 Y_T Y_K + r_8 Y_B Y_K + r_9 Y_K Y_F) \\
F_8 &= \frac{dY_S}{dt} = r_7 Y_T Y_K + r_8 Y_B Y_K + r_9 Y_K Y_F \\
F_9 &= \frac{dY_F}{dt} = -r_9 Y_F Y_K \\
F_{10} &= \frac{dY_W}{dt} = r_9 Y_F Y_K
\end{aligned} \tag{6}$$

with initial conditions, $Y_B(0) = Y_{B0}$, $Y_T(0) = Y_{T0}$, $Y_D(0) = Y_{D0}$, $Y_M(0) = Y_{M0}$, $Y_A(0) = Y_{A0}$, $Y_G(0) = Y_{G0}$, $Y_K(0) = Y_{K0}$, $Y_S(0) = Y_{S0}$, $Y_F(0) = Y_{F0}$, and $Y_W(0) = Y_{W0}$.

Our main objective is to maximize biodiesel production with minimal production costs. So, we formulated the cost function as follows

$$J[z] = \int_{t_0}^{t_f} [W_1 z^2 - W_2 Y_B^2] dt \tag{7}$$

where W_1 represents the weight constant for the cost function's benefit with $W_1 > 0$, while W_2 stands for the penalty multiplier. We want to identify the best control z^* such that

$$J(z^*) = \min\{J(z) : z \in Z\}$$

Z represents the permissible control set defined by

$$\begin{aligned}
Z &= \{z(t) : z(t) \text{ is measurable with } 0 \leq z(t) \leq 1, \\
&\quad t \in [t_0, t_f]\}
\end{aligned}$$

Here, we employ the minimum principle by Pontryagin³⁶ to determine z^* .

The Hamiltonian can be written as

$$\mathcal{H} = W_1 z^2 - W_2 Y_B^2 + \sum_{n=1}^{10} \Psi_n F_n \tag{8}$$

where $\Psi_1, \Psi_2, \dots, \Psi_{10}$ are adjoint variables, and F_1, F_2, \dots, F_{10} are functions defined in eq 6.

Now, when the optimal control z^* and the solution $(Y_B^*, Y_T^*, Y_D^*, Y_M^*, Y_A^*, Y_G^*, Y_K^*, Y_S^*, Y_F^*, Y_W^*)$ of the corresponding system (5) minimizes $J(z)$ over Z , there will be adjoint variables $\Psi_1, \Psi_2, \dots, \Psi_{10}$ that satisfy the following equations

$$\begin{aligned}
\frac{d\Psi_1}{dt} &= 2W_2 Y_B + \Psi_1(r_2 Y_D + r_4 Y_M + r_6 Y_G + r_8 Y_K) \\
&\quad + M_c \left(1 - \frac{2Y_B}{B_{\max}} \right) z - \Psi_2 r_2 Y_D \\
&\quad + \Psi_3(r_2 Y_D - r_4 Y_M) + \Psi_4(r_4 Y_M - r_6 Y_G) \\
&\quad - \Psi_5(r_2 Y_D + r_4 Y_M + r_6 Y_G + r_8 Y_K) \\
&\quad + \Psi_6 r_6 Y_G + \Psi_7 r_8 Y_K - \Psi_8 r_8 Y_K \\
\frac{d\Psi_2}{dt} &= -\Psi_1 r_1 Y_A + \Psi_2 r_1 Y_A + \Psi_2 r_7 Y_K - \Psi_3 r_1 Y_A + \Psi_5 r_1 Y_A \\
&\quad - \Psi_6 r_7 Y_K + \Psi_7 r_7 Y_K - \Psi_8 r_7 Y_K \\
\frac{d\Psi_3}{dt} &= \Psi_1 r_2 Y_B - \Psi_1 r_3 Y_A - \Psi_2 r_2 Y_B + \Psi_3 r_2 Y_B + \Psi_3 r_3 Y_A \\
&\quad - \Psi_4 r_3 Y_A - \Psi_5 r_2 Y_B + \Psi_5 r_3 Y_A \\
\frac{d\Psi_4}{dt} &= \Psi_1 r_4 Y_B - \Psi_1 r_5 Y_A - \Psi_3 r_4 Y_B + \Psi_4(r_4 Y_B + r_5 Y_A) \\
&\quad - \Psi_5(r_4 Y_B - r_5 Y_A) - \Psi_6 r_5 Y_A \\
\frac{d\Psi_5}{dt} &= -\Psi_1(r_1 Y_T + r_3 Y_D + r_5 Y_M) + \Psi_2 r_1 Y_T - \Psi_3 r_1 Y_T \\
&\quad + \Psi_3 r_3 Y_D - \Psi_4(r_3 Y_D - r_5 Y_M) \\
&\quad + \Psi_5(r_1 Y_T + r_3 Y_D + r_5 Y_M) - \Psi_6 r_5 Y_M \\
\frac{d\Psi_6}{dt} &= (\Psi_1 - \Psi_4 - \Psi_5 + \Psi_6) r_6 Y_B \\
\frac{d\Psi_7}{dt} &= \Psi_1 r_8 Y_B + \Psi_2 r_7 Y_T - \Psi_3 r_8 Y_B - \Psi_6 r_7 Y_T \\
&\quad + \Psi_7(r_7 Y_T + r_8 Y_B + r_9 Y_F) \\
&\quad - \Psi_8(r_7 Y_T + r_8 Y_B + r_9 Y_F) + \Psi_9 r_9 Y_F - \Psi_{10} r_9 Y_F \\
\frac{d\Psi_8}{dt} &= 0 \\
\frac{d\Psi_9}{dt} &= (\Psi_7 - \Psi_8 + \Psi_9 - \Psi_{10}) r_9 Y_K \\
\frac{d\Psi_{10}}{dt} &= 0.
\end{aligned} \tag{9}$$

along with the transversality condition, $\Psi_i(t_f) = 0$ for all $i = 1, 2, \dots, 10$. From 7 we can write the Hamiltonian as

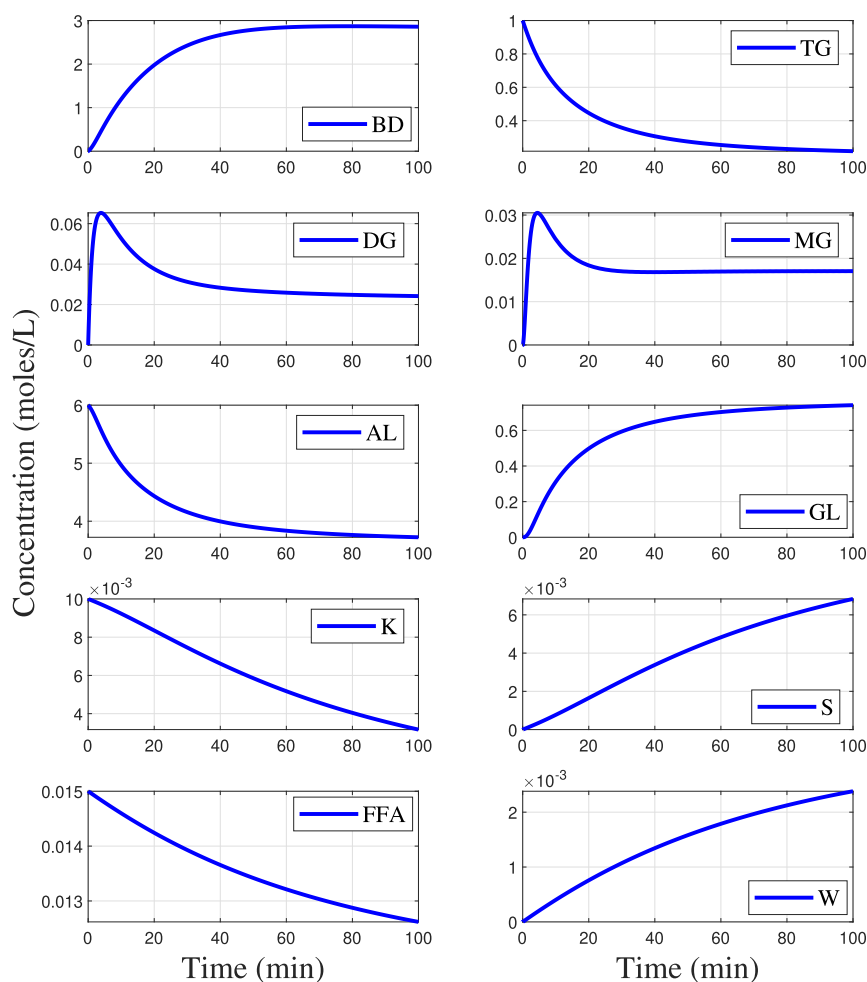


Figure 3. Variation of concentration over time at a fixed temperature in base-catalyzed transesterification, utilizing parameters outlined in Table 1. Here, ultrasound frequency $H = 50$ kHz, vessel diameter $d = 1$ m, and methanol-to-oil ratio is 6:1.

$$\begin{aligned} \mathcal{H} &= W_1 z^2 - W_2 Y_B^2 + \sum_{n=1}^{10} \Psi_n F_n \\ &= W_1 z^2 + \Psi_1 z M_c Y_B \left(1 - \frac{Y_B}{B_{\max}} \right) + \text{terms not} \\ &\quad \text{containing } z \end{aligned} \quad (10)$$

Now, according to the necessary condition of the Pontryagin minimum principle,³⁶ optimal control variable z^* will satisfy the condition

$$\frac{\partial \mathcal{H}}{\partial z^*} = 0 \quad (11)$$

From eq 9 and 10, we have

$$\frac{\partial \mathcal{H}}{\partial z^*} = 2W_1 z^* + M_c Y_B \left(1 - \frac{Y_B}{B_{\max}} \right) (\Psi_1) = 0 \quad (12)$$

which implies that

$$z^* = \frac{M_c Y_B \left(1 - \frac{Y_B}{B_{\max}} \right) (-\Psi_1)}{2W_1} \quad (13)$$

Since the standard control is bounded ($0 \leq z \leq 1$), we can

write

$$z^* = \begin{cases} 0, & \frac{M_c Y_B \left(1 - \frac{Y_B}{B_{\max}} \right) (-\Psi_1)}{2W_1} \leq 0; \\ \frac{M_c Y_B \left(1 - \frac{Y_B}{B_{\max}} \right) (-\Psi_1)}{2W_1}, & 0 < \frac{M_c Y_B \left(1 - \frac{Y_B}{B_{\max}} \right) (-\Psi_1)}{2W_1} < 1; \\ 1, & \frac{M_c Y_B \left(1 - \frac{Y_B}{B_{\max}} \right) (-\Psi_1)}{2W_1} \geq 1. \end{cases} \quad (14)$$

or in compact form, we can write z^* as

$$z^* = \max \left(0, \min \left(1, \frac{M_c Y_B \left(1 - \frac{Y_B}{B_{\max}} \right) (-\Psi_1)}{2W_1} \right) \right) \quad (15)$$

Based on the minimum principle by Pontryagin,³⁶ adjoint variables satisfy the following equation

$$\frac{d\Psi_j}{dt} = -\frac{\partial H}{\partial Y_j}, \quad j = 1, 2, \dots, 10 \quad (16)$$

where $Y_j \equiv (Y_B^*, Y_T^*, Y_D^*, Y_M^*, Y_A^*, Y_G^*, Y_K^*, Y_S^*, Y_F^*, Y_W^*)$, and the necessary conditions that satisfy the optimal control z^* are

$$\mathcal{H}(Y_j, z^*, \Psi_j, t) = \min(Y_j, z, \Psi_j, t), \quad j = 1, 2, \dots, 10 \quad (17)$$

Utilizing relation (16), we obtain the whole adjoint system denoted by eq 9.

4. RESULTS

In this section, we employed numerical simulations using the ode45 solver to analyze the system dynamics. This enabled us to acquire more profound insight into how the transesterification reaction behaves when a KOH catalyst is present during the production of biodiesel.

Due to the disparate polarities of methanol and Jatropha oil, they are almost immiscible, leading to substantial mass transfer resistance between the two substances. To reduce this mass transfer limitation, we have used ultrasound frequency and compared the biodiesel yield with control and without control through the minimum principle by Pontryagin with Hamiltonian. In the biodiesel production process, we employ the molar ratio of Jatropha-oil-to-methanol, along with ultrasound, to investigate their respective effects. Also, we analyzed the biodiesel yield dependency on the size of the reaction vessel.

Figure 3 represents the concentration trajectories of biodiesel, soap, glycerol, and some other intermediates of transesterification reaction utilizing a 50 kHz ultrasound frequency, a 1 m vessel diameter, and a 6:1 methanol-to-Jatropha-oil molar ratio. Various reaction constants and B_{\max} are taken from Table 3. It is evident from the figure that the production of biodiesel and glycerol gradually increased from 0 to 40 min, and after 40 min, the production remained constant until the end of the reaction. Also, a small amount of soap is produced with increasing time.

Figure 4 represents the effect of the length of the vessel diameter in the reaction kinetics. Based on the figure, it is evident that reducing the vessel diameter results in enhanced biodiesel production, holding the ultrasonic frequency at 50 kHz and the methanol-to-oil molar ratio at 6:1. This is because increasing the vessel diameter for a fixed ultrasound frequency will produce less turbulence between methanol and jatropha oil, and decreasing the diameter will produce more turbulence.

Therefore, a reduction in the vessel diameter leads to a decrease in mass transfer resistance, resulting in an increased biodiesel production yield. Hence, the vessel's diameter plays a pivotal role in biodiesel production. In this case, the considerable diameter of the vessel is 1 m.

The molar ratio of methanol-to-Jatropha-oil is one of the key factors in determining biodiesel production.³⁷ In Figure 5, the influence of methanol-to-Jatropha-oil molar ratio has been shown for 4:1, 5:1, 6:1, and 7:1. At 6:1, we get 90% biodiesel in less than 60 min at a 50 kHz frequency of ultrasound. Initially,

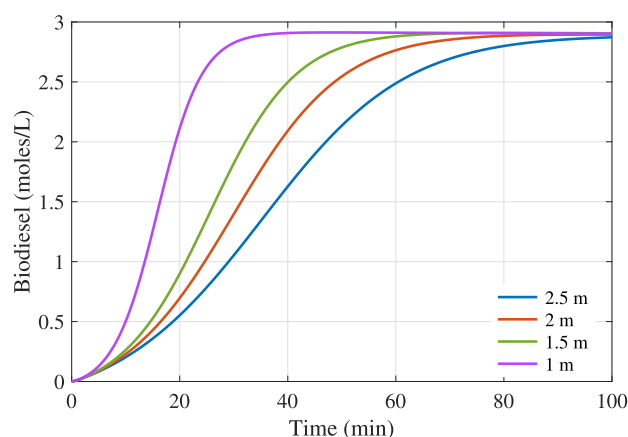


Figure 4. Concentration profile of biodiesel production for different diameters of the reaction vessel with ultrasound frequency $H = 50$ kHz and AL: TG of 6:1.

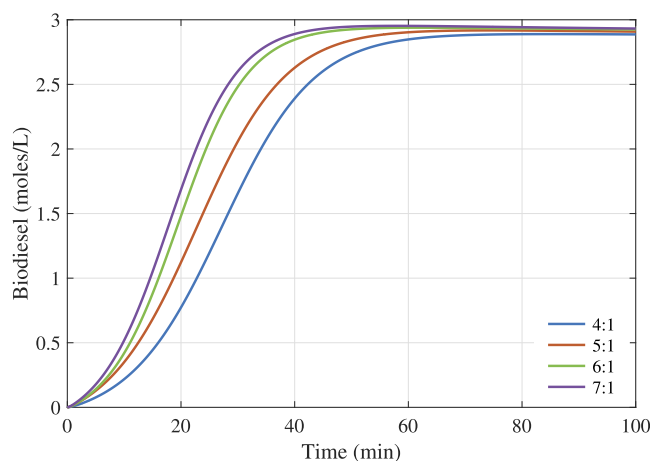


Figure 5. Biodiesel concentration profiles with varying methanol-to-triglyceride molar ratios. Here, ultrasound frequency $H = 50$ kHz and vessel diameter $d = 1$ m.

the biodiesel production increases at the 7:1 molar ratio with a 50 kHz ultrasound frequency, but after 50 min, the yield conversion is almost the same as that for the 6:1 molar ratio. It can also be observed from Figure 7b that there is no need to increase the molar ratio of methanol-to-oil beyond 6:1, as there is no further increase in production. To reduce costs, we have chosen a 6:1 molar ratio of methanol and Jatropha oil for the synthesis of biodiesel in our research work.

Figure 6 shows how biodiesel production varies with the ultrasound frequency. The reaction rate increases significantly when the frequency of ultrasound is increased up to 50 kHz. For a further increment of frequency of ultrasound, concentration of biodiesel decreases over time. Elevating the ultrasound frequency to 60 kHz or 70 kHz initially boosts biodiesel production. However, after 47 min of reaction time, biodiesel yields start to decrease, leading to an undesirable drop in biodiesel concentration over time. This occurs as a result of the fact that a higher frequency of ultrasound increases the volatility of the reacting methanol. The vaporization of methanol from the reaction vessel leads to a reduction in the quantity of one of the reactants and also interferes with the desired methanol-to-triglycerides ratio. According to the figure, achieving the highest biodiesel output requires a 50 kHz ultrasonic frequency in

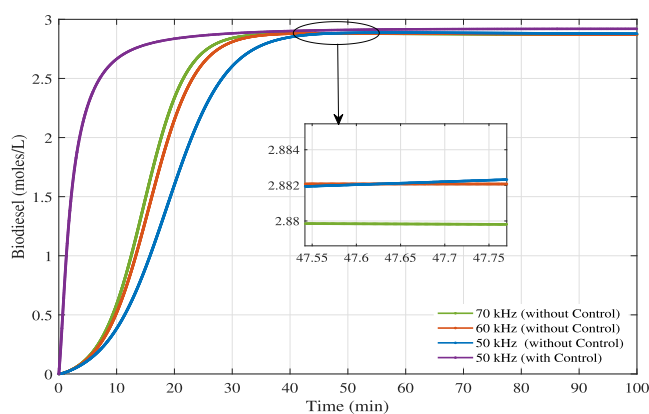


Figure 6. Variation in biodiesel yield concentration with ultrasound frequencies at a fixed methanol-to-oil molar ratio of 6:1 and vessel diameter of 1 m with and without control.

conjunction with a 6:1 methanol-to-Jatropha-oil ratio and 1 m of vessel diameter.

Figure 7a depicts the mutual effect of ultrasound frequency and vessel diameter, whereas Figure 7b depicts the mutual effect of the molar ratio and ultrasound frequency for biodiesel synthesis. These figures demonstrate how biodiesel conversion varies on ultrasound frequency, molar ratio of methanol and Jatropha oil, and vessel diameter.

Although mixing intensity plays a crucial role in biodiesel synthesis together with the molar ratio of reactants and vessel size, the control of ultrasound frequency holds substantial importance for the optimization of the intended outcomes. As triglyceride and methanol are incapable of mixing because of their nonpolar and polar properties, initially a greater ultrasound frequency is required to overcome the mass transfer limitation in the transesterification reaction. Figure 8a clearly shows that, after 8 min, less control over ultrasound is necessary. This is because the biodiesel, which is produced after 8 min, will serve as a medium for the mixture of the two reactants, functions as a continuous state for reactants, and minimizes mass transfer limitation. Eventually, at almost 40 min, a very low frequency of ultrasound is needed because, at this point, the reaction has almost finished. Based on the aforementioned discussion, it is apparent that, despite the substantial impact of mixing intensity

and other kinetic factors on biodiesel synthesis, controlling the ultrasound frequency throughout the reaction process has a crucial role in optimizing biodiesel production. Figure 6 presents a comparison of biodiesel concentration with and without the incorporation of an ultrasound control technique. Through the application of optimal control on ultrasound frequency, the constraint of mass transfer limitation is nearly eradicated, achieving a yield conversion of more than 97% in less than 40 min of reaction time. Figure 8b shows the biodiesel yield conversion with respect to time. According to this figure, the control operation enhances the biodiesel yield by approximately 6%.

5. DISCUSSION AND CONCLUSIONS

This study presents a mathematical model for the transesterification reaction between methanol and Jatropha oil to produce biodiesel with few basic assumptions. It demonstrates how mixing intensity through the ultrasonic effect, molar ratio, and vessel diameter have significant effects on successful reaction progression. It is clear from the Reynolds number formulation that its relationship with ultrasonic frequency is one of direct proportion; that is, the Reynolds number rises with the increase of ultrasound frequency. Mathematically, we have seen that the creation of biodiesel will reach a certain threshold level if the ultrasonic frequency is increased. Therefore, biodiesel production increases if the Reynolds number is raised. Biodiesel concentration was determined under varying reaction conditions, including the methanol-to-triglycerides molar ratio and ultrasound frequency. This study reveals the significance of optimization of the ultrasonic effect and addressing mass transfer resistance as key factors in transesterification. Therefore, the impacts of ultrasound and vessel size, which are responsible for the creation of turbulence within the vessel, are the most important parameters for affecting the mass transfer. It can be demonstrated that delivering ultrasound to the system has a significant effect on the economic production of biodiesel by assuming a control technique on the ultrasound effect.

Through a comparative analysis of biodiesel yield conversion under varying ultrasound frequencies, we achieved a 90% biodiesel yield within 60 min, when we set the ultrasound frequency to 50 kHz, the molar ratio of methanol and Jatropha oil to 6:1, and the vessel diameter to 1 m without any control.

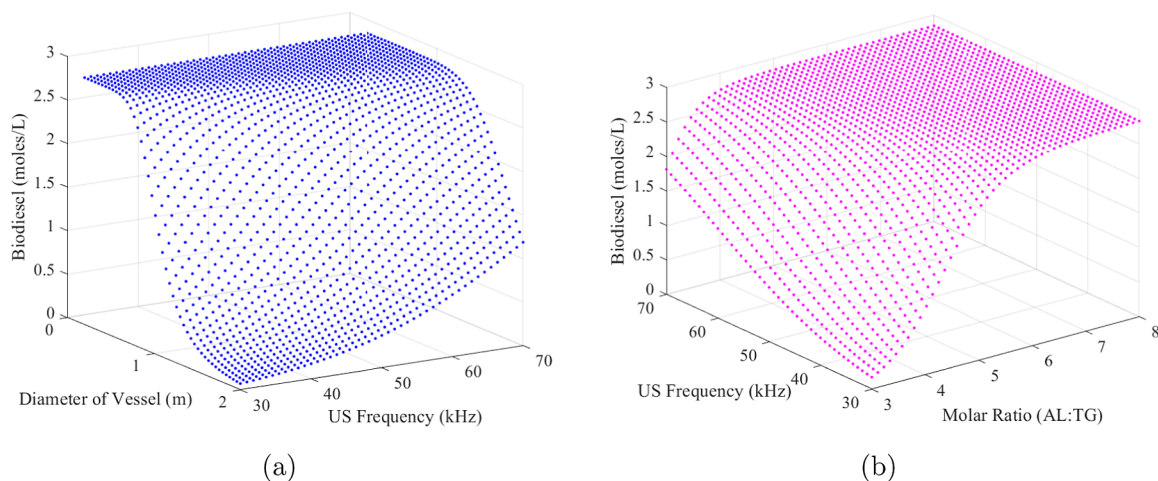


Figure 7. Biodiesel yield concentration for different (a) vessel diameters and ultrasound frequencies and (b) molar ratio of methanol-to-triglyceride and ultrasound frequencies.

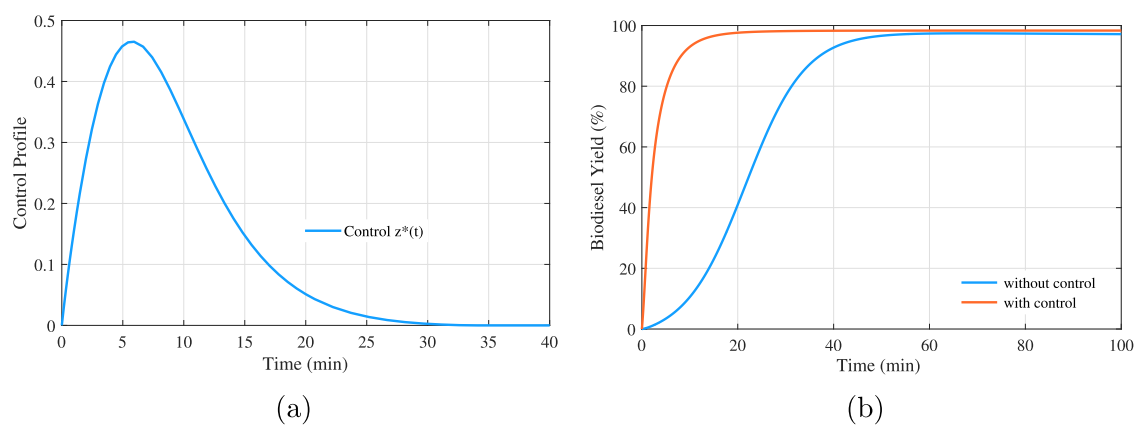


Figure 8. (a) Time-dependent optimal control profile for ultrasound frequency. (b) Biodiesel yield conversion with respect to time with and without control at 50 kHz ultrasound frequency, 6:1 methanol-to-Jatropha-oil molar ratio, and 1 m of vessel diameter.

But by employing a control theoretical approach in conjunction with 50 kHz ultrasound frequency, while maintaining the same molar ratio and vessel diameter, we have achieved more than 97% biodiesel yield within a reduced time frame of just 50 min. The present study shows the efficacy of ultrasound frequency in biodiesel production to remove the constraints of mass transfer limitation to a great extent. It is also comparable with the results of biodiesel production using a mechanical stirrer. Since in this case the energy input is less than that of the mechanical stirrer, this method is superior to the study with the mechanical stirrer.

5.1. Recommendation. It is recommended that experimental scenarios be conducted within the suggested biodiesel production process to assess its effects on ultrasonic control. This would enable experimental researchers to generate accurate predictions of system parameters for the production of biodiesel in advance, which we have achieved from our analytical, numerical, and control theoretical approach.

AUTHOR INFORMATION

Corresponding Author

Priti Kumar Roy – Department of Mathematics, Jadavpur University, Kolkata 700032, India; orcid.org/0000-0001-7454-4367; Phone: +91 9432095603; Email: pritiyu@gmail.com

Authors

Xianbing Cao – School of Mathematics and Statistics, Beijing Technology and Business University, Beijing 100048, China
 Sk Mosaraf Ahammed – Department of Mathematics, Jadavpur University, Kolkata 700032, India
 Siddhartha Datta – Department of Chemical Engineering, Jadavpur University, Kolkata 700032, India
 Jahangir Chowdhury – Department of Applied Science, RCC Institute of Information Technology, Kolkata 700015, India

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.4c01729>

Notes

The authors declare no competing financial interest.

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