Single-Step Ultrasonic Synthesis of Biodiesel from Crude *Jatropha curcas* Oil

Hanif A. Choudhury
Center for Energy, Indian Institute of Technology Guwahati, Guwahati, Assam 781 039, India

Pulkit Srivastava
Dept. of Chemical Engineering, National Institute of Technology (NIT), Tiruchirapalli, Tamil Nadu 620 015, India

Vijayanand S. Moholkar
Center for Energy, Indian Institute of Technology Guwahati, Guwahati, Assam 781 039, India

Dept. of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, Assam 781 039, India

DOI 10.1002/aic.14371

A novel single-step process with chlorosulfonic acid catalyst for ultrasonic biodiesel synthesis using feedstock with high free fatty acid content is investigated.Jatropha curcas oil has been used as the model feedstock with methanol as alcohol. The distinct merit of chlorosulfonic acid is that it catalyzes both esterification and transesterification reactions. Moreover, chlorosulfonic acid also counteracts inhibition caused by water formed during esterification, which is the cause for very slow kinetics of acid catalyzed transesterification. In addition, sonication of the reaction mixture also causes strong micromixing and emulsification that enhances the transesterification kinetics. Statistical optimization of the process shows 93% yield for 8.5 wt % catalyst, 20:1 alcohol to oil molar ratio and temperature of 333 K. Peculiar feature of this process is that high yield is seen at moderate temperature and molar ratio, which are much smaller than that for conventional sulfuric acid catalyzed processes. The activation energy for the process (57 kJ/mol) is at least 3× lower than the energy for sulfuric acid catalyzed transesterification. The thermodynamic analysis reveals that the net Gibbs energy change for the single-step process is almost same as that for sulfuric acid catalyzed process. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 1572–1581, 2014

Keywords: biodiesel, reaction kinetics, ultrasound, transesterification, acid catalyst

Introduction

Biodiesel which essentially is methyl/ethyl ester of fatty acid has shown high potential for being a renewable and carbon neutral liquid transportation fuel.[1] The feedstock for biodiesel production is vegetable oil. For third world countries like India, which face shortage of edible oils, economic production of biodiesel is feasible only with cheap feedstocks of nonedible vegetable oils or animal fats or waste greases.[2] However, major problem with these feedstocks for the transesterification reaction is their high free fatty acid (FFA) content. *Jatropha curcas* oil has been identified as a potential source of nonedible oil feedstock for biodiesel production in India.[3] Numerous articles have been published that report synthesis of biodiesel from *Jatropha curcas* oil with diverse catalysts and protocols. Extensive research has also been carried out in genetic modifications of the plant to increase the oil content of the seeds and higher yield of seed per plant. Several state-of-the-art reviews[4–7] have been published that give detailed account of literature in this area. Crude Jatropha oil available from farmers and villager has high FFA content up to 10–20%. Due to this, the conventional base catalyzed transesterification process cannot be carried out with *Jatropha curcas* oil, as it leads to formation of soap. Biodiesel synthesis from *Jatropha curcas* oil is, therefore, carried out in two-step method, where initially, the FFAs are converted to esters in presence of acid catalyst, and this is followed by conversion of triglycerides (TG) to esters with base catalyst. Numerous studies have adopted this methodology with mechanical agitation of reaction mixture.[8–14] Changeover from acid to base catalyst in the two-step esterification/transesterification leads to longer overall process time. Use of acid catalyst in both steps requires very long process time, due to very slow kinetics of acid catalyzed transesterification. A solution for enhancement of the acid catalyzed transesterification is ultrasound irradiation of the reaction mixture. The ultrasound wave propagates through the medium as a longitudinal wave that generates sinusoidal variation in the bulk pressure of the system. The fluid elements of the medium undergo small amplitude and high frequency oscillation that generates strong microconvection (or

---

Additional Supporting Information may be found in the online version of this article.

Correspondence concerning this article should be addressed to V. S. Moholkar at vmoholkar@iitg.ernet.in.

micromixing) in the system. Moreover, the bulk pressure variation gives rise to phenomenon of cavitation, which is nucleation, growth, and implosive transient collapse of gas or vapor bubbles. The transient collapse of bubble is adiabatic, and temperature and pressure inside the bubble reaches extreme ($\sim$5000 K and $\sim$500 bar) during collapse. Transient cavitation has both physical and chemical effects on the system.[15] The physical effect is generation of strong microconvection by oscillatory motion of fluid elements in close vicinity of bubble (termed as microturbulence) and high-pressure amplitude shock waves. The chemical effect is in terms of generation of radicals from dissociation of solvent vapor trapped in the bubble at the moment of transient collapse. In our previous article,[16] we have discriminated between physical and chemical effects of ultrasound and cavitation on transesterification reaction system. It has been revealed in this article that the principal effect of ultrasound and cavitation on the transesterification system is of physical nature. The strong microconvection generated by ultrasound and cavitation results in formation of fine emulsion between oil and methanol phases. This emulsification generates very high interfacial area leading to faster reaction kinetics. Water formed during the esterification process strongly inhibits the catalytic activity of acid catalyst (especially H_2SO_4) for transesterification.[2,17] Therefore, intermediate purification of the reaction mixture, after esterification, is necessary to enhance kinetics of the ensuing transesterification reaction. For large scale processes, this step can significantly increase the fixed and operating cost, in addition to increasing the overall batch process time.

In this article, we have presented a novel approach for single-step ultrasonic synthesis of biodiesel from high FFA containing vegetable oil like *Jatropha curcas* using chlorosulfonic acid as catalyst. This catalyst brings about *in situ* removal of water formed during esterification process, thus, counteracting the inhibition. The esterification/transesterification process with chlorosulfonic acid thus obviates the need of intermediate purification of reaction mixture, giving high yields of biodiesel (comparable to those using base catalyst) in reasonable reaction periods. We have studied this process using a statistical experimental design (Box–Behnken method and fitted quadratic model with Analysis of Variance) to determine the optimum reaction conditions. Moreover, we have also done Arrhenius and thermodynamic analysis of the process to determine the kinetics and thermodynamic parameter such as pseudo first-order kinetic constant, activation energies, enthalpy, and entropy change. This analysis has revealed interesting features of the chlorosulfonic acid catalyzed esterification/transesterification process.

Theoretical Contemplation

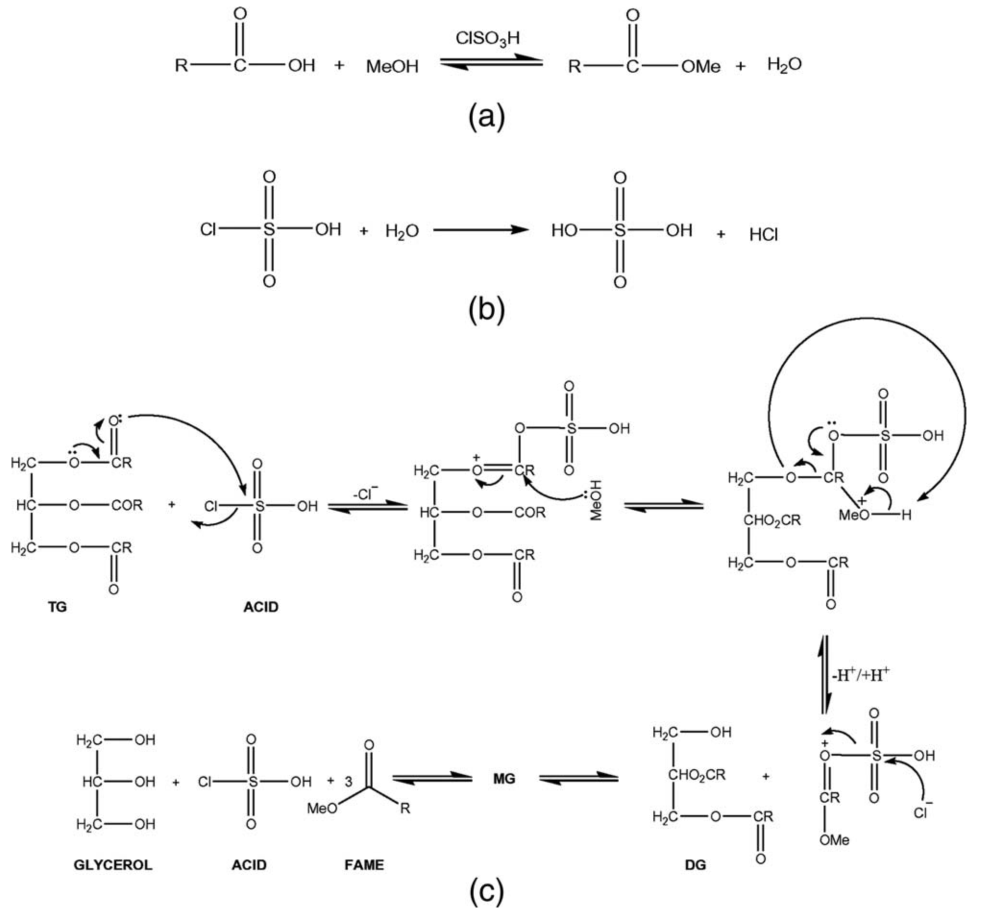
Before proceeding to the experimental section, we present herewith the theoretical contemplations that formed basis of this study. As noted in the preceding section, the major problem with acid catalyzed esterification of FFAs in *Jatropha curcas* oil is the inhibition of the catalyst caused by the water formed in the esterification process. A discussion is given below regarding the mechanism through which this inhibition occurs.

Inhibition of acid catalyst during transesterification

The mechanism of the inhibition of homogenous acid catalyst in presence of water has been explained by Liu et al.[18] and Ataya et al.[19] During esterification process, the protonation of the carbonyl oxygen is a fast quasiequilibrium step. The subsequent nucleophilic attack of alcohol on the protonated carboxylic acid, resulting in formation of tetrahedral intermediate, is the rate determining step. Dissociation of sulfuric acid in aqueous medium results in formation of H_3O^+ (hydroxonium) ion and HSO_4^- (bisulfate) ions. As H_3O^+ is strongly acidic species, the water content of the medium does not change the H_3O^+ concentration, or the rate limiting step. The inhibition effect of water on H_2SO_4 catalyst could be an effect of two causes, viz. decrease in acid strength and/or loss of catalyst accessibility. The protons H^+ generated from dissociation of H_2SO_4 can form either H_3O^+ ion or $CH_3OH_2^+$ (methoxonium) ion. Bronsted acid theory suggests $CH_3OH_2^+$ to be more acidic than H_3O^+.[20] However, according to solvation chemistry of protons, it is the solvation state of the protons that determines the strength of strong acid like H_2SO_4 than the extent of dissociation. Greater solvation of protons results in lowering of its chemical and catalytic activity. Comparing among $CH_3OH_2^+$ and H_3O^+ ions, without taking into consideration solvation characteristics, a lower acidity for $CH_3OH_2^+$ is expected due to higher inductive effect of methyl group, which is in contradiction with the Brønsted acid theory. The solvation state of proton is determined by contribution of all solvating molecules. Strong hydrogen bond networks formed by water molecule can delocalize the charge on the H_3O^+ ion, thus stabilizing it. Comparing on this basis, the $CH_3OH_2^+$ ion (where steric hindrance of $-CH_3$ group comes into picture) has less ability to form hydrogen bonds. Second, comparing the solvation generated by H_2O and CH_3OH molecules, we see that H_2O is a better donor of electron pair than methanol. Therefore, contribution to solvation of protons by water molecule is much higher than methanol. Greater enthalpy release occurs during solvation of H_3O^+ and CH_3OH^+ in water than in methanol. On this basis, Liu et al.[18] and Pines and Fleming [21] hypothesize water as proton sponge that accommodates protons inside a self-assembled water network with lower entropic state. Conversely, the solvation of proton by methanol molecules is hindered due to their smaller orientational polarizability, and lesser symmetry of the CH_3OH molecule than H_2O.

Ataya et al.[19] have put the reduction in catalytic activity of H_2SO_4 in a slightly different context on the basis of hypothesis of Gileadi and Kirowa-Eisner,[22] which states that water molecule in presence of methanol acts as scavenger for proton to form H_3O^+ cation. Therefore, in an emulsion of reaction mixture comprising of CH_3OH, H_2O, H_2SO_4, and any FFA, a core of H_3O^+ cations and their sulfate anions can form micelles, with FFA molecule on the exterior. The hydrophilic end of FFA (containing the $-OH$ tail) would be close to H_3O^+ core and the hydrocarbon end in the methanol phase. This phenomenon will result in formation of micelles of FFA$-H_3O^+$ with acid cores in the polar CH_3OH phase. However, these micelles are shielded from the bulk methanol phase. Formation of FFA$-H_3O^+$ micelles in the TG phase has also been proposed by Lotero et al.,[2] who showed that acidic species are distributed in both alcohol and oil (or TG) phase. The micelle in the TG phase shields and reduces the accessibility of the acid catalyst by the TG molecules.

In summary, solvation of protons with water, higher energy is need for protonation of carbonyl oxygen in the FFA or TG by H_3O^+ proton carrier. Protonation of FFA/TG results in greater reduction in entropy that generates more



Scheme 1. **(A) Reaction of chlorosulfonic acid-induced esterification process.**

(B) *In situ* removal of water formed during esterification by chlorosulfonic acid. (C) Chemical mechanism of chlorosulfonic acid induced transesterification process.

geometric configuration for nucleophilic attack of methanol, thus increasing the collision efficiency.

Counteraction of water inhibition during biodiesel synthesis by chlorosulfonic acid

Biodiesel synthesis in presence of chlorosulfonic acid occurs in three steps as given below.

Esterification. As shown in Scheme 1A, reaction of a FFA molecule with methanol in presence of chlorosulfonic acid catalyst results in formation of an ester and a water molecule.[23]

In situ Removal of Water by Chlorosulfonic Acid. The water produced in the esterification process reacts with chlorosulfonic acid molecule to produce H_2SO_4, as shown in Scheme 1B.[24] Dissociation of H_2SO_4 thus produced can generate additional protons that catalyze the esterification/transesterification reaction. However, generation of H_2SO_4 is accompanied by *in situ* removal of water molecule that solvate the H_3O^+ ion and reduce its activity. Although H_2O formed during esterification breaks the chlorosulfonic acid, resulting species of H_2SO_4 is strongly acidic that maintains the overall catalyst activity more or less constant. The mechanism of H_2SO_4 catalyzed transesterification has been explained in our earlier article[15] is also provided is Supporting Information with this article.

Transesterification. Scheme 1C shows the mechanism proposed for transesterification of TG in presence of chlorosulfonic acid catalyst. The initial transesterification is induced by scission of S—Cl bond of the chlorosulfonic acid creating electropositive center on sulfur, which is attacked by the nonbonding electron of carbonyl oxygen. This generates an intermediate "A" with electrophillic center at the carbonyl-carbon of TG, which is followed by nucleophilic attack of methanol on carbonyl-carbon of TG. Rearrangement of intermediates with abstraction of proton by TG moiety produces diglyceride (DG) and catalyst bound ester. The attack of Cl^- ion on this intermediate regenerates chlorosulfonic acid catalyst with release of one fatty acid methyl ester (FAME) molecule. Consecutive reaction of DG and monoglyceride (MG) then further produces two more molecules of FAME and regenerates the acid catalyst.

With this conjectures and contemplation devised our transesterification experiments using statistical design.

Materials and Methods

Materials

Jatropha curcas oil (in crude form) was procured from local farmers. This oil was used as received without any further purification or refining. The acid value and saponification value of the oil was determined as 21.57 and 201.2 mg KOH/g, respectively, using standard methods.[25] The average molecular weight of oil was determined as 932 g/mol using the equation $M=\frac{(56.1\times3\times1000)}{(\mathrm{SV}-\mathrm{AV})}$, where 56.1 is the molecular weight of KOH, whereas number 3 denotes the number of fatty acids per TG.[26] Other chemicals used in experiments

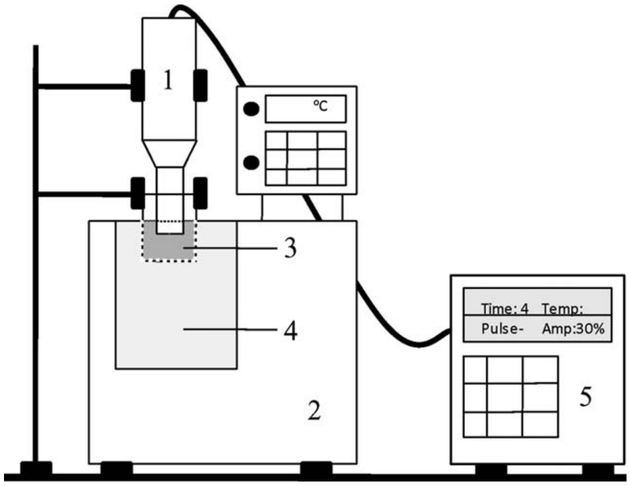


Figure 1. Schematic diagram of the experimental setup: (1) ultrasound probe; (2) refrigerated and heating bath circulator; (3) reaction mixture; (4) water in the refrigerated bath; and (5) ultrasonic processor.

are methanol (Merck, India, AR grade 99%) and chlorosulfonic acid (Sigma Aldrich, India, AR grade 90%). These chemicals were also used as received without any further treatment.

Experimental setup

The schematic diagram of the experimental setup is given in Figure 1. Transesterification reaction was carried out in 100-mL beakers made of borosilicate glass. To conduct reactions at different temperatures, the beaker was submerged in the reservoir of a refrigerated circular bath (Jeio Tech, Model: Lab Companion RW 0525G) filled with water. The temperature of the water in reservoir was maintained at different levels, viz. 303, 318, and 333 K. Internal circulation of water was provided so as to maintain a constant temperature. The temperature of reaction mixture was monitored with a digital thermometer, and was found to be same as that of the water in the reservoir. A programmable microprocessor-based ultrasonic processor (Sonics and Materials, Model: VCX 500) was used for sonication. This processor had operating frequency of 20 kHz with a sonicator probe of 25-mm diameter. It was fabricated from high grade titanium alloy (Ti-6Al-4V). The processor was facilitated with automatic tuning and frequency control and automatic amplitude compensation. The amplitude for all the experiments was set to 25% corresponding to a power input of 125 W (theoretical maximum power). The actual acoustic pressure amplitude was determined using calorimetric measurement with methanol as the medium as 1.6 bar (corresponding to net energy consumption of 1.1 W).[27]

Experimental Protocol

Base Case Experiment. Initially, as the base case of experiments, esterification/transesterification was carried out using mechanical stirring of reaction mixture (a photograph of this setup has been provided in Supporting Information Figure S1). This reaction was conducted at 338 K for 16 h with 20:1 alcohol to oil molar ratio and catalyst concentration of 5 wt % oil with total reaction volume of 15 mL. The progress of the reaction was monitored by withdrawing aliquots (500 μL) of reaction mixture every 4 h and analyzing for conversion of TG and FFA with ^{1}H NMR (Varian 400 MHz FT-NMR) spectrometry with $CDCl_3$ as solvent and tetramethylsilane as internal standard.[28,29] This method gives the gross conversion (X) of TG and FFA to their corresponding ester. We have termed this conversion as percentage yield of FAME (100 X) and all kinetic and thermodynamic analysis has been made on this basis. The results of base case experiments revealed percentage FAME yield of ~90% after 16 h given in Figure 2. The slow kinetics of acid catalyzed biodiesel synthesis, as mentioned earlier, is evident from this result.

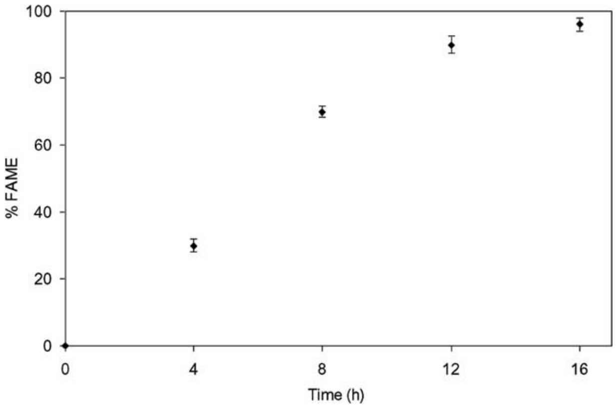


Figure 2. Results of the control experiments with mechanical stirring (reaction parameters: alcohol to oil molar ratio = 20:1, temperature = 338 K, catalyst concentration = 5 wt % oil, agitation speed = 300 rpm).

Statistical Experimental Design (Single-Step Esterification-Transesterification). Further experiments were carried out using sonication (or ultrasound irradiation) of the reaction mixture (total reaction volume of 15 mL) so as to boost its kinetics, as noted earlier. These experiments were devised as per the statistical experimental design (Box–Behnken method). The following experimental parameters (or independent variables) have been chosen for optimization: catalyst loading (C), temperature (T), and alcohol to oil molar ratio (R). The experiments were conducted with a fixed sonication time of 4 h, based on our initial experiments. The actual and coded values of different experimental parameters (i.e., levels of the independent variables) used in the Box–Behnken design are shown in Table 1. The response variable, that is, % FAME yield (or percentage conversion of TG and FFA), was fitted with a full quadratic model (given in Eq. 1) to correlate it to the experimental parameters or independent variables

Table 1. Experimental Range and Levels of Independent Variables

Independent Variables (or Factors)	Symbol Coded	Levels of Factors Coded Value (Actual Value)		
Catalyst concentration (wt % oil)	C	−1 (1)	0 (5)	+1 (9)
Temperature (K)	T	−1 (303)	0 (318)	+1 (333)
Alcohol to oil molar ratio (M)	M	−1 (10:1)	0 (20:1)	+1 (30:1)

Table 2. Box–Behnken Experimental Design Matrix

Sl. No.	Catalyst (wt % Oil)	Molar Ratio	Temperature (K)	% FAME Yield	Fitted % FAME Yield
1	1 (−1)	10 (−1)	318 (0)	15.09 ± 0.67	12.01
2	5 (0)	10 (−1)	333 (+1)	69.91 ± 1.67	65.04
3	9 (+1)	20 (0)	303 (−1)	59.99 ± 1.29	52.05
4	1 (−1)	20 (0)	333 (+1)	24.68 ± 0.75	32.61
5	5 (0)	30 (+1)	303 (−1)	32.70 ± 0.68	37.56
6	5 (0)	20 (0)	318 (0)	80.12 ± 3.5	76.66
7	5 (0)	30 (+1)	333 (+1)	53.56 ± 0.51	54.48
8	1 (−1)	30 (+1)	318 (0)	27.67 ± 0.49	18.80
9	1 (−1)	20 (0)	303 (−1)	15.20 ± 1.11	19.20
10	9 (+1)	30 (+1)	318 (0)	53.65 ± 1.14	56.72
11	9 (+1)	10 (−1)	318 (0)	56.87 v 0.87	65.73
12	5 (0)	20 (0)	318 (0)	76.56 ± 1.46	76.66
13[a]	**9 (+1)**	**20 (0)**	**333 (+1)**	**95.4 ± 1.03**	**91.4**
14	5 (0)	10 (−1)	303 (−1)	30.13 ± 1.19	29.2
15	5 (0)	20 (0)	318 (0)	73.31 ± 3.5	76.66

[a] The bold values indicate experimental set with the highest FAME yield.

$$Y=\beta_0+\sum_{i=1}^{3}\beta_i x_i+\sum_{i=1}^{3}\beta_{ii}x_i^2+\sum_{i=1}^{2}\sum_{j=i+1}^{3}\beta_{ij}x_i x_j \qquad (1)$$

Notations are as follows: Y = response variable (i.e., % FAME yield); β_0 = constant; β_i, β_{ii}, and β_{ij} = regression coefficients; x_i and x_j = coded independent variables. The Box–Behnken statistical design of experiments, devised using Minitab 15 software (trial version) comprises of 15 sets with (three factors and three levels) with different combinations of parameters. The experimental conditions in these sets are given in Table 2, whereas exact composition of reaction mixture in each set is given in Supporting Information Table S1. The progress of the esterification-transesterification reaction was monitored by withdrawing 500-μL aliquots of the reaction mixtures every 30 min. To quench the reaction, the aliquots were immediately mixed with 1 mL 0.05 N NaOH and centrifuged at 6000 rpm for 10 min to separate the acid catalyst and aqueous phase (comprising of glycerol and alcohol). The organic layer was then analyzed by ^{1}H NMR to determine the percentage yield of FAME.

Conventional Two-Step Experiments. As noted in previous section, one of the contemplations underlying this study was that chlorosulfonic acid causes *in situ* removal of water formed during esterification process, thus eliminating the water inhibition to acid catalyzed transesterification. To ascertain this conjecture, we have also carried out biodiesel synthesis with crude *Jatropha curcas* oil with conventional two-step approach of separate esterification and transesterification, with intermediate purification of the reaction mixture to remove water formed during esterification. In these set of experiments, the esterification experiments were carried out for 1 h using H_2SO_4 catalyst (3 wt % oil) at 338 K and 15:1 molar ratio. These values were decided on the basis of our earlier study.[17] This process essentially converts almost all FFA (>95%) into corresponding esters. This reaction mixture was neutralized by addition of 0.05 M NaOH solution. The organic layer was separated and washed three times with hot water to remove all traces of acid and alcohol. This layer was dried on activated silica to remove traces of water. This layer is essentially FFA free Jatropha oil containing TGs. The transesterification of this layer with sonication was then carried out using chlorosulfonic acid catalyst. The experimental parameters (viz. molar ratio and catalyst concentration) used in this transesterification reaction were essentially same as the optimized conditions obtained from statistical experimental design, as described in previous section. The reaction temperature, however, was varied at three levels, viz. 303, 318, and 333 K for kinetic and thermodynamic analysis with a fixed reaction time of 3 h. The comparison of yield and kinetics of these experiments with the single step experiments (based on statistical design described in previous section) give an estimate of the beneficial effect of *in situ* removal of water by chlorosulfonic acid.

Table 3. Statistical Analysis of Experimental Results—Estimated Regression Coefficients for % FAME Yield

Term	Coefficients	SE Coeff	*t*-Stat	*p*-Value
Constant (β)	76.66	5.2	14.73	0.
Temperature (T)	13.19	3.18	4.14	0.
Molar ratio (M)	−0.55	3.18	−0.17	0.869
Catalyst (C)	22.9	3.18	7.19	0.001
Temperature × Temperature (T^2)	−9.79	4.69	−2.09	0.091
Molar ratio × Molar ratio (M^2)	−20.29	4.69	−4.33	0.008
Catalyst × Catalyst (C^2)	−18.05	4.69	−3.85	0.012
Temperature × Molar ratio (TM)	−4.73	4.5	−1.05	0.342
Temperature × Catalyst (TC)	6.48	4.5	1.44	0.21
Molar ratio × Catalyst (MC)	−3.95	4.5	−0.88	0.421

Determination of Transesterification Kinetics. Synthesis of biodiesel in single step reactions with chlorosulfonic acid catalyst occurs in four consecutive and reversible reactions steps. The first step is the reaction of FFA with methanol to give one molecule of FAME and water. The chlorosulfonic acid reacts with water molecule to yield H_2SO_4 which itself can catalyze both esterification and transesterification steps. The ensuing transesterification step begins with the reaction of TG and methanol to produce diglycerides (DG) and one molecule of FAME; this is followed by reaction of DG with methanol yields monoglycerides (MG) and another molecule of FAME. In final step, MG reacts with methanol to yields third molecule of FAME and one mole of glycerol. Thus, four molecules of FAME (one from esterification of an FFA molecule and three from transesterification of a TG molecule) and one molecule each of glycerol is formed after completion of the reaction. In our analysis, we have determined the kinetic constant of the overall reaction, without accounting for the intermediate steps.

Table 4. Statistical Analysis of Experimental Results—Analysis of Variance (ANOVA) for Transesterification of Jatropha Oil using Ultrasound

Source	DF	Sq SS	Adj SS	Adj MS	*F*	*p*-Value
Regression	9	8629.32	8629.32	958.81	11.8	0.007
Linear	3	5593.	5593.	1864.33	22.95	0.002
Square	3	2716.32	2716.32	905.44	11.15	0.012
Interaction	3	319.99	319.99	106.66	1.31	0.368
Residual error	5	406.15	406.15	81.23	–	–
Lack-of-Fit	3	382.95	382.95	127.65	11.	0.084
Pure error	2	23.2	23.2	11.6	–	–
Total	14	9035.47			–	–

$R^2 = 0.955$; R^2 (adj) $= 0.874$.

As the FFA content of the *Jatropha curcas* oil is rather low, it is the kinetics of transesterification step that governs the overall process time and yield of biodiesel. Based on our previous studies, we have assumed the transesterification reaction to follow pseudo first-order kinetics and the equation fitted to the conversion data is

$$\ln(1-X) = -kt \tag{2}$$

where X = conversion of TG at any time t. Plot of $-\ln(1-X)$ vs. t gives the kinetic constant k as the slope.

Determination of Activation Energy (Arrhenius Plot). A relationship between the specific reaction rate constant (k), absolute temperature (T), and the energy of activation (E_a) is given by the Arrhenius equation as: $k = A \times \exp(-E_a/RT)$ where A is the frequency factor and R is universal gas constant (J/mol/K).

To determine the activation energy of the single-step process (involving both esterification and transesterification), experiments were conducted at three different temperatures viz. 303, 318, and 333 K. The catalyst concentration and molar ratio in these experiments were same as the global optimum values obtained from statistical experimental design. To deduce the change in activation energy from conventional double-step process to single-step process, experiment were conducted in two-step procedure at same three temperatures as that of the single-step process. The plot of ln (k) vs. $1/T$ gives slope equal to $(-E_a/R)$ from which activation energy can be determined.

Result and Discussion

Statistical analysis

Single step transesterification experiments: as noted earlier, these experiments were based on Box–Behnken statistical design. The results of the 15 sets of experiments in this design are given in Table 2. The quadratic regression model fitted to these results using Eq. 1 is given below

$$Y = 76.66 + 13.17\,T - 0.55\,M + 22.90\,C - 9.97\,T^2 - 20.29\,M^2 - 18.05\,C^2 - 4.73\,T \times M - 3.95\,M \times 6.48\,T \times C \tag{3}$$

where, T, M, and C indicate temperature, molar ratio, and catalyst concentration, respectively. The significance of coefficients corresponding to each parameter is estimated by the t-test and p-value given in the Table 3. Table 4 shows the ANOVA for the quadratic model. The values of FAME yield predicted by this model are in excellent agreement with the experimental values. The overall R^2 value of the regression is 0.95, which reveals excellent fit of the model to the experimental data and point that 95.5% of the effect on the yield for chlorosulfonic acid catalyst was explained by the variation in process variables. The fitted quadratic equation is in terms of the coded values of the parameters and not in absolute values. A p-value of <0.05 of any coefficient (either linear or quadratic interaction) designates it as significant or insignificant. On this basis, molar ratio is relatively insignificant than the other two parameters, viz. temperature and catalyst concentration. Moreover, the interaction effects between process parameters were found to be insignificant. The response surface plots depicting variation in FAME yield as a function of any two process parameters (as independent variable parameters), with the value of third process parameter (fixed parameter) held at its center point in the Box–Behnken design are given in Supporting Information Figure S3. These plots are representatives of the interactive effect of the two process parameter on the yield. It could be seen from surface plots that the yield shows a maxima for a particular combination of two process parameters that are treated as variables for the plot. Table 5 gives the exact values of the process parameter in each of the three surface plots (either from combination of temperature-molar ratio, molar ratio-catalyst concentration, and catalyst concentration and temperature) for which maxima in yield is obtained.

Inspection of the Table 5, which gives the optimum combination of process parameters for the highest yield in the three surface plots, reveals that the optimum value of molar ratio (whether considered as fixed or variable parameter) for the

Table 5. Statistical Analysis of Experimental Results—Analysis of Surface Plots (Values of Variable Parameters for Maximum Yield for Center Point Value of Third Parameter)

Fixed Parameter (Center Point Value)	Variable Parameter		FAME Yield (%)
Catalyst concentration = 5 wt % oil	Temperature = 328.4 K	Molar ratio = 19.1	81.3
Temperature = 318 K	Molar ratio = 19.3	Catalyst concentration = 7.6 wt % oil	84
Molar ratio = 20:1	Temperature = 332.1 K	Catalyst concentration = 8.2 wt % oil	92

GLOBAL OPTIMUM: Catalyst = 8.35354, Molar ratio = 17.89, Temp = 333 K, and Yield = 93%.

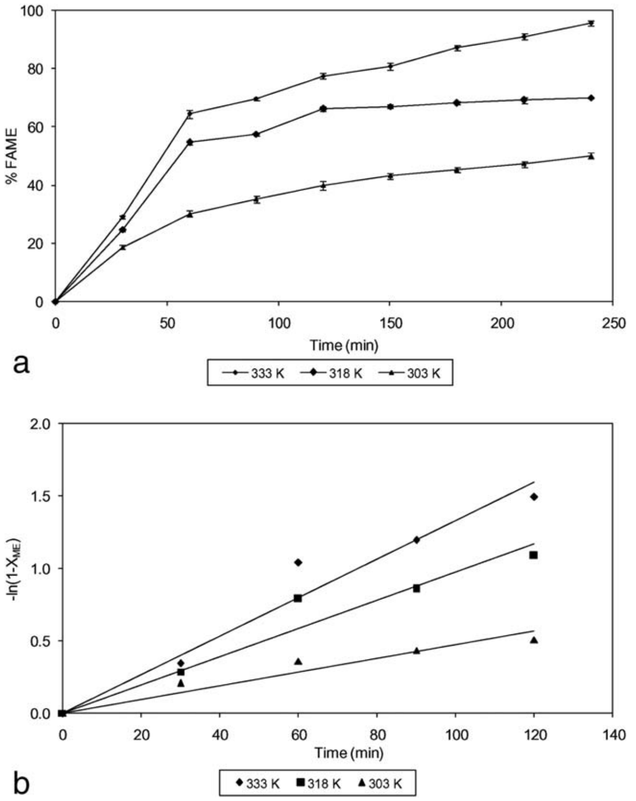


Figure 3. Kinetic analysis of single-step transesterification process under optimum conditions.

(A) Time history of FAME yield at different reaction temperature. (B) Fitting of pseudo first-order kinetic model fitted to the conversion data for determination of kinetic constants. Best fit equations:Best fit equations: For 303 K, $y = 0.00472\ x$, $R^2 = 0.92$; For 318 K, $y = 0.00976\ x$, $R^2 = 0.94$; For 333 K, $y = 0.0133\ x$, $R^2 = 0.954$.

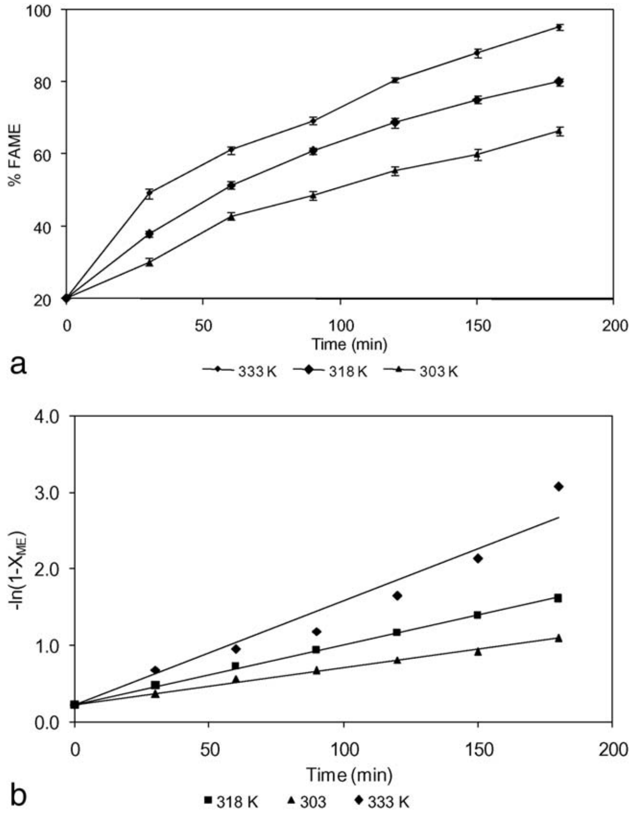


Figure 4. Kinetic analysis of the two-step transesterification process.

(A) Time history of FAME yield at different reaction temperatures. (B) Fitting of pseudo first-order kinetic model to the conversion data. Best fit equations: For 303 K, $y = 0.00485\ x + 0.22$, $R^2 = 0.99$; For 318 K, $y = 0.00787\ x + 0.22$, $R^2 = 0.99$; For 333 K, $y = 0.0137\ x + 0.22$, $R^2 = 0.945$.

highest yield remains the same. The highest yield of 92% is obtained when both transesterification temperature and catalyst concentration is high. The temperature (332.1 K) for the highest yield is close to the boiling point of methanol. The yield drops marginally if either temperature or the catalyst concentration is lowered. An interesting observation is that the molar ratio required for high yield with chlorosulfonic acid catalyst (20:1) is more than double that of the molar ratio required for sulfuric acid catalyst in a two-step process. The probable causes for large requirement of alcohol are as follows:

The transesterification process in case of chlorosulfonic acid begins with activation of carbon–oxygen bond of the carbonyl carbon of TG by acid rather than direct protonation for the case of H_2SO_4 as reported by Lotero et al.[2] (for convenience of the reader mechanism has been given as Supporting Information Figure S2). The intermediate "A" formed after the activation of carbon–oxygen bond by chlorosulfonic acid is a very large molecule. As a result the methanol molecule trying to access the electrophillic center is likely to face significant steric hindrance. Therefore, large quantities of alcohol are required to over populate the hindered site and to drive the reversible transesterification reaction toward forward direction.

All the water formed during the esterification of FFA may not be removed from the reaction medium by chlorosulfonic acid immediately. Thus, traces of water present in the reaction mixture at any point of time can drive the reversible reaction of acid catalyzed aqueous hydrolysis. To counteract this large amount of alcohol is required to drive forward the esterification reaction.

The global maximum of the FAME yield (93%) in reaction time of 4 h as per the quadratic regression model is obtained for conditions: catalyst concentration ≈8.35, molar ratio ≈18:1, and temperature ≈333 K. These conditions are much moderate as compared to those reported in literature for acid catalyzed transesterification reactions (e.g., temperature >373

Table 6. Kinetic and Thermodynamic Analysis of Transesterification Process—Arrhenius analysis

	Single Step Process		Double Step Process	
Temperature (K)	Pseudo First-Order Kinetic Constant (min^{-1})	Activation Energy (kJ/mol)	Pseudo First-Order Kinetic Constant (min^{-1})	Activation Energy (kJ/mol)
333	0.0133	57.33	0.0137	31.29
318	0.0096		0.0078	
303	0.0047		0.0048	

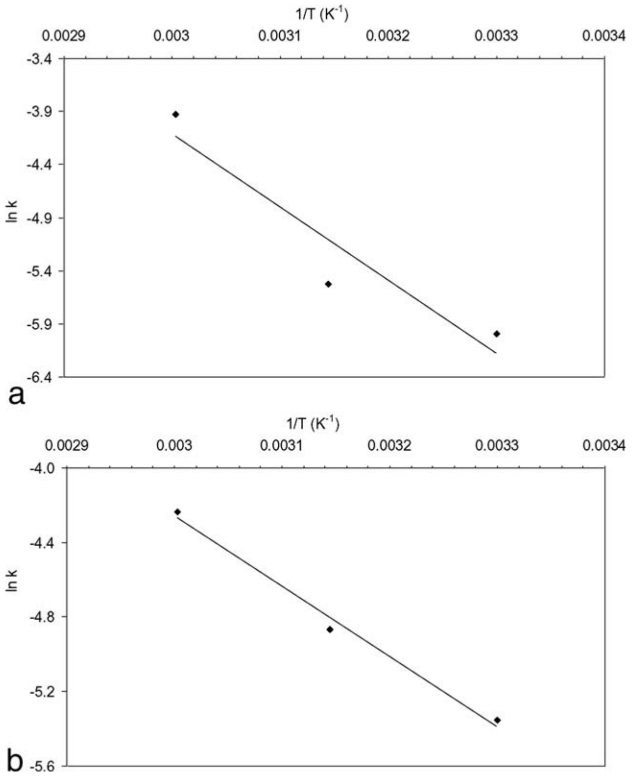


Figure 5. Arrhenius plot for determination activation energy of transesterification process.

(A) Single-step process, Best fit: $y = -6895.1\ x + 16.57$, $R^2 = 0.89$; (B) Double-step process with intermediate water removal after esterification, Best fit: $y = -3764.2\ x + 7.0357$, $R^2 = 0.99$.

K and reaction time of 20 h as reported by Freedman et al.[30]). Same argument holds for molar ratio of 20:1 for optimum yield. This value is also much lower than the molar ratios exceeding 50 reported in literature for acid catalyzed transesterification.[31] Table 2 gives comparative analysis of FAME yield results in different experimental set that helps us to deduce the relative influence of each of the process parameters under study.

Comparison of results of experimental Sets 4 and 9 reveals the influence of temperature. With a low catalyst concentration of 1 wt % and molar ratio of 20:1, the FAME yield show as 75% increase as the temperature is doubled from 303 to 333 K.

Comparison of results of Sets 1and 11 reveals that increasing catalyst concentration from 1 to 9 wt % can take yield to significantly high value of ~66% for an alcohol molar ratio of 10:1.

Comparison of results of Sets 2 and 7 reveals the insignificant influence of the molar ratio. Even with 3× increase in molar ratio (from 10:1 in Set 2 to 30:1 in Set 7) at catalyst concentration of 5 wt % and temperature of 333 K, the FAME yield in these sets shows a trivial difference of ~20% (i.e., 53.56% yield in Set 7 and 69.91% yield in Set 2). Similar trend is also seen from the result of experimental Set 1 and 8.

The above results clearly identify catalyst concentration and temperature as the most significant variable of the process affecting FAME yield. The highest yield is therefore seen for catalyst concentration of 9 wt %, temperature of 333 K, and moderate molar ratio of 20:1. Lower FAME yield at very large molar ratio of 30:1 could be a consequence of rather dilute acid concentration is aqueous phase.

Intrinsic Kinetics vs. Mass Transfer. Comparison of biodiesel yield with ultrasound under optimized conditions of molar ratio, temperature, and catalyst concentration with the base case experiment (under mechanical agitation) reveals that fine emulsification generated by microconvection induced by ultrasound and cavitation reduces the mass transfer limitations, thus boosting the gross kinetics of the reaction. As regards to physical mechanism of the ultrasonic process, we have shown in our earlier articles[17,32–34] that convection generated by ultrasound/cavitation in methanol phase is mainly responsible for formation of emulsion. Given this result, in the Box–Behnken experimental design, the net interfacial area between oil/methanol phases is likely to be in the reactions in which the highest for molar ratio of 30:1 is used. However, as discussed earlier, the FAME yield in Box–Behnken experiments reduces at very high molar ratio of 30:1. These results clearly reveal the relative roles of mass transfer and intrinsic kinetics on the reaction system. Subsequent to formation of fine emulsion with ultrasonication, the reaction system is controlled by intrinsic kinetics, which in turn depends on catalyst concentration (that determines the activation energy) and the temperature. It should also be pointed out that probability of interaction between acid and TG molecule reduces at higher molar ratios that reduce the concentration of acid (this effect is most marked at the highest molar ratio of 30). This factor also contributes

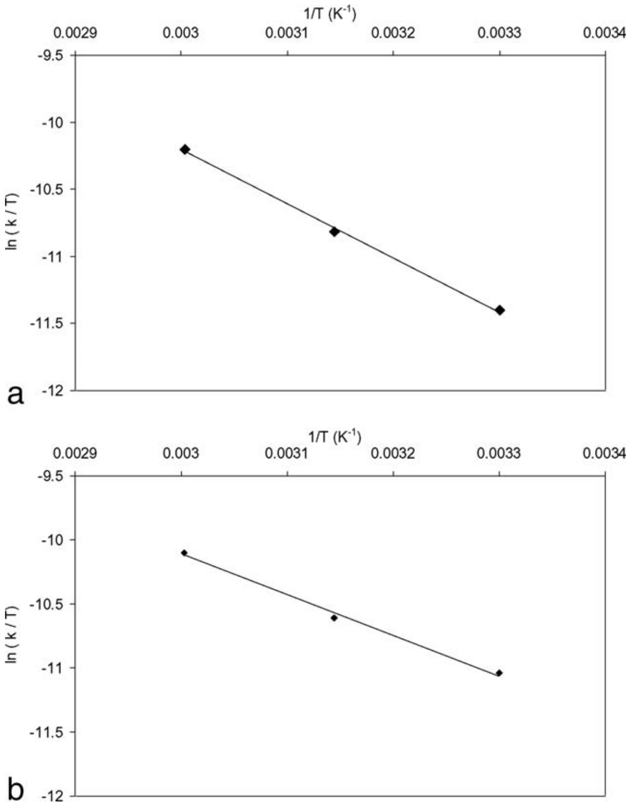


Figure 6. Eyring plots to determine change in enthalpy (Δ*H*) and change in entropy (Δ*S*) during transesterification process.

(A) Single-step process, Best fit: $y = -4023\ x + 1.8621$, $R^2 = 0.99$; (B) Double-step process (with intermediate removal of water after esterification), Best fit: $y = -3168.8\ x - 0.603$, $R^2 = 0.99$.

Table 7. Kinetic and Thermodynamic Analysis of Transesterification Process—Thermodynamic Analysis

	Single Step Process			Double Step Process		
Temperature (K)	ΔH (kJ/mol)	$-\Delta S$ (kJ/mol K)	ΔG (kJ/mol)	ΔH (kJ/mol)	$-\Delta S$ (kJ/mol K)	ΔG (kJ/mol)
333	33.45	0.18	94.07	28.65	0.2	96.1
318			91.34			93.06
303			88.61			90.02

to lowering of the gross kinetics of the process leading to smaller yields.

Kinetic and Thermodynamic Analysis. The kinetics of the single step biodiesel synthesis was studied at three temperatures for global optimum conditions of molar ratio and catalyst concentrations. The time history of the FAME yield and the pseudo first-order kinetic model fitted to the data is shown in Figure 3. To compare kinetic behavior of the single step and double-step process experiment have been conducted with two-step procedure also. The temperature of experiment of the second step (i.e., transesterification) was kept at same values, that is, 303, 318, and 333 K. The catalyst concentration and molar ratio were same as the global optimum of single-step process with fixed reaction time of 3 h. The time history of the conversion of the TG in the transesterification process and the pseudo first-order kinetic model fit to the kinetic data are shown in Figure 4. Table 6 lists the pseudo first-order kinetic constants for both single- and double-step experiments at three temperatures, whereas Figure 5 shows the corresponding Arrhenius plots. It could be seen that the kinetic constants for both single- and double-step processes at different temperatures do not show significant variation. The activation energy for single step biodiesel synthesis is 57.3 kJ/mol, and interestingly it shows a reduction of ~40% to 31.3 kJ/mol for the double-step process. We attribute this reduction of activation energy to almost complete absence of water in the reaction mixture in the transesterification in double-step process. Contrary to this, despite *in situ* water removal by chlorosulfonic acid, some traces of water may be left out in the reaction mixture in the single-step process, which contribute to catalyst inhibition and rise in the activation energy.

Comparing the values of activation energy for chlorosulfonic acid catalyzed biodiesel synthesis with the activation energy observed with that of H_2SO_4 catalyzed biodiesel synthesis gives a very interesting result. In our own experiments with H_2SO_4 catalyzed esterification/transesterification of crude *Jatropha curcas* oil, we have observed an activation energy of 169.4 kJ/mol.[17] Freedman et al. have also reported relatively higher activation energies (>80 kJ/mol) for acid catalyzed transesterification reactions.[30] However, with chlorosulfonic acid catalyst, the activation energies are 3× lower than the H_2SO_4 catalyzed biodiesel synthesis. Although at this juncture, we are unable to provide a justification for result, this effect is likely to be consequence of basic difference in the mechanism of transesterification reaction with H_2SO_4 and chlorosulfonic acid catalyst.

Thermodynamic Analysis. Using the result of kinetic analysis, we have also determined the thermodynamic characteristic of the single-step and double-step process of biodiesel synthesis with chlorosulfonic acid catalyst. For this purpose, we have used the Eyring equation

$$\ln\frac{k}{T} = -\frac{\Delta H}{R}\frac{1}{T} + \ln\frac{k_b}{h} + \frac{\Delta S}{R} \qquad (4)$$

where k is the rate constant at temperature T, and ΔH and ΔS are the changes in enthalpy and entropy of the reaction system, respectively. k_b, h, and R are Boltzmann, Planck, and universal gas constant, respectively. ΔH and ΔS for the process can be determined from the slope and y-intercept of the Eyring plot ($\ln k/T$ vs. $1/T$). The Eyring plots for the single- and double-step process are shown in Figure 6. Table 7 lists the value of ΔH, ΔS, and ΔG (Gibbs energy change) for the process, determined using equation $\Delta G = \Delta H - T\Delta S$. A slight increase of ΔH is seen for single-step process as compared to the double step, which in turn is compensated by a lower activation energy for double-step process. Again, a possible cause of this trend is absence of water in the reaction mixture for the double-step process. The result of these inverse variations is that the overall Gibbs energy change for both single-step and double-step protocol is practically same.

Conclusions

In this article, we have reported a novel single-step process for ultrasonic biodiesel synthesis from high FFA feedstocks like *Jatropha curcas* oil using chlorosulfonic acid catalyst. The principal merit of chlorosulfonic acid is that it catalyzes both esterification and transesterification reactions, and also counteracts the inhibition caused by water formed during esterification. Due to this peculiar feature, the conventional two-step process of esterification-transesterification can be combined. The overall reaction time as well as process infrastructure required for new single-step process is obviously much smaller than the conventional double-step process. Statistical optimization of the process shows 93% yield in just 4 h at moderate conditions of 8.5 wt % catalyst, 20:1 alcohol to oil molar ratio, and temperature of 333 K. The activation energy for the process is at least 3× lower than the activation energy reported for H_2SO_4 catalyst. However, the thermodynamic analysis reveals that the net Gibbs energy change for the single-step process is almost same as that for the conventional double-step process. Consequently, it is expected that the chlorosulfonic acid-based biodiesel manufacture process will have significantly lesser capital investment as well as production cost than the conventional biodiesel processes. In summary, the chlorosulfonic acid-based process for biodiesel has shown encouraging results and high potential, which deserve more in-depth investigation.

Acknowledgments

Hanif A. Choudhury gratefully acknowledges receipt of financial assistance from Ministry of New and Renewable Energy, Government of India through National Renewable

Energy Fellowship during this work. Authors acknowledge analytical facilities provided by Central Instrumental Facility of I.I.T. Guwahati.

Literature Cited

1. Ma F, Hanna MA. Biodiesel production: a review. *Bioresour Technol.* 1999;70:1–15.
2. Lotero E, Liu Y, Lopez DE, Suwannakarn K, Bruce DA, Goodwin JG Jr. Synthesis of biodiesel via acid catalysis. *Ind Eng Chem Res.* 2005;44:5353–5363.
3. Government of India. *Report of the Committee on Development of Biofuels, Planning Commission*. New Delhi: Government of India, April 2003.
4. Yusuf NNAN, Kamarudin SK, Yaakub Z. Overview on the current trends in biodiesel production. *Energy Convers Manag.* 2011;52: 2741–2751.
5. Jain S, Sharma MP. Prospects of biodiesel from Jatropha in India: a review. *Renew Sust Energy Rev.* 2010;14:763–771.
6. Koh MY, Ghazi TIM. A review of biodiesel production from Jatropha curcas L. oil. *Renew Sust Energy Rev.* 2011;15:2240–2251.
7. Pandey VC, Singh K, Singh JS, Kumar A, Singh B, Singh RP. Jatropha curcas: a potential biofuel plant for sustainable environmental development. *Renew Sust Energy Rev.* 2012;16:2870–2883.
8. Berchmans HJ, Hirata S. Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids. *Bioresour Technol.* 2008;99:1716–1721.
9. Jain S, Sharma MP. Kinetics of acid base catalyzed transesterification of Jatropha curcas oil. *Bioresour Technol.* 2010;101:7701–7706.
10. Jain S, Sharma MP. Biodiesel production from Jatropha oil. *Renew Sust Energy Rev.* 2010;14:3140–3147.
11. Tiwari AK, Kumar A, Raheman H. Biodiesel production from Jatropha oil (Jatropha curcas) with high free fatty acids: an optimized process. *Biomass Bioenergy.* 2007;31:569–575.
12. Patil PD, Deng S. Optimization of biodiesel production from edible and non-edible vegetable oils. *Fuel.* 2009;88:1302–1306.
13. Lu H, Liu Y, Zhou H, Yang Y, Chen M, Liang B. Production of biodiesel from Jatropha curcas L. *oil. Comput Chem Eng.* 2009;33: 1091–1096.
14. Corro G, Tellez N, Ayala E, Marinez-Ayala A. Two-step biodiesel production from Jatropha curcas crude oil using SiO2·HF solid catalyst for FFA esterification step. *Fuel.* 2010;89:2815–2821.
15. Shah YT, Pandit AB, Moholkar VS. Cavitation Reaction Engineering. New York: Plenum Press, 1999.
16. Kalva A, Sivasankar T, Moholkar VS. Physical mechanism of ultrasound assisted synthesis of biodiesel. *Ind Eng Chem Res.* 2009;48: 534–544.
17. Choudhury HA, Malani RS, Moholkar VS. Acid catalyzed biodiesel synthesis from Jatropha oil: mechanistic aspects of ultrasound intensification. *Chem Eng J.* 2013;231:262–272.
18. Liu Y, Lotero E, Goodwin JG Jr. Effect of water on sulfuric acid catalyzed esterification. *J Mol Catal A Chem* 2006;245:132–140.
19. Ataya F, Dube MA, Ternan M. Acid-catalyzed transesterification of Canola oil to biodiesel under single- and two-phase reaction conditions. *Energy Fuel.* 2007;21:2450–2459.
20. Sadek H, Elamayem MSA, Elgeheit MA. Acid hydrolysis of ethyl acetate in presence of glycol or glycerol. *Suom Kemistil.* 1963;63:115–123.
21. Pines E, Fleming GR. Proton transfer in mixed water-organic solvent solutions: correlation between rate, equilibrium constant, and the proton free energy of transfer. *J Phys Chem.* 1991;95:10448–10457.
22. Gileadi E, Kirowa-Eisner E. Electrolytic conductivitys—the hopping mechanism of the proton and beyond. *Electrochim Acta.* 2006; 51:6003–6011.
23. Xuarez L, Rodriguez Z, Gonzalez R, Mesa M, Pellon R. New conditions for synthesis of diethyl acetonedicarboxylate. *Revista CENIC, Ciencias Quimicas.* 1994–1995;25–26(1–3):13–14.
24. Cremlyn RJ. *Chlorosulfonic Acid A Versatile Reagent*. United Kingdom: Royal Society of Chemisty, 2002.
25. Nielsen SS. Food Analysis Laboratory Manual, 4th ed. New York: Springer-Verlag, 2010.
26. Deng X, Fang Z, Liu Y. Ultrasonic transesterification of Jatropha curcas L. oil to biodiesel by a two-step process. *Energy Convers Manag.* 2010;51:2802–2807.
27. Sivasankar T, Paunikar AW, Moholkar VS. Mechanistic approach to enhancement of the yield of a sonochemical reaction. *AIChE J.* 2007;53:1132–1143.
28. Gelbard G, Brès O, Vargas RM, Vielfaure F, Schuchardt UF. 1H nuclear magnetic resonance determination of the yield of the transesterification of rapeseed oil with methanol. *J Am Oil Chem Soc.* 1995;72:1239–1241.
29. Knothe G. Analytical methods used in the production and fuel quality assessment of biodiesel. *Trans ASAE.* 2001;44:193–200.
30. Freedman B, Butterfield RO, Pryde EH. Transesterification kinetics of soybean oil. *J Am Oil Chem Soc.* 1986;63:1375–1380.
31. Zheng S, Kates M, Dube MA, McLean DD. Acid-catalyzed production of biodiesel from waste frying oil. *Biomass Bioenergy.* 2006;30: 267–272.
32. Parkar PA, Choudhary HA, Moholkar VS. Mechanistic and kinetic investigations in ultrasound assisted acid catalyzed biodiesel synthesis. *Chem Eng J.* 2012;187:248–260.
33. Choudhury HA, Chakma S, Moholkar VS. Mechanistic insight into sonochemical biodiesel synthesis using heterogeneous base catalyst. *Ultrason Sonochem.* 2014;21:169–181.
34. Choudhury HA, Goswami PP, Malani RS, Moholkar VS. Ultrasonic biodiesel synthesis from crude *Jatropha curcas* oil with heterogeneous base catalyst: mechanistic insight and statistical optimization. *Ultrason Sonochem.* In press. dx.doi.org/10.1016/j.ultsonch.2013.10.023.

Manuscript received Aug. 28, 2013, revision received Nov. 25, 2013, and final revision received Jan. 11, 2014.