

Chapter 2

Physical and Chemical Mechanisms of Ultrasound in Biofuel Synthesis

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Abstract Physical and chemical mechanisms ultrasound-assisted processes as related to the synthesis of biofuels are reviewed. Ultrasound and its secondary effect of cavitation have physical and chemical effects on a reaction system, which can contribute to enhancement of the kinetics and yield. In this chapter, a mechanistic insight into the ultrasound assisted biofuels synthesis is given by coupling simulations of cavitation bubble dynamics with experimental data. The physical effect of ultrasound and cavitation is through intense micro-convection in the system that gives marked improvements in the mass transfer of the system. The chemical effect is through generation of highly reactive radicals through transient cavitation that induce or accelerate chemical reactions. Chemical effects include thermal decomposition of the solvent vapor molecules in the cavitation bubble resulting in generation of smaller molecular species that also affect chemistry of the process. Raising the static pressure of the reaction system above ultrasound pressure amplitude in the system helps to discriminate between physical and chemical effects of ultrasound and cavitation. Biofuels systems considered in this chapter are the pretreatment of biomass, biodiesel synthesis with acid/base and homogeneous/heterogeneous catalysts, extraction of microalgal lipids, bioconversion of crude glycerol from biodiesel industry to value added products and desulfurization of the fuel. Among the physical effects of ultrasound and cavitation, micro-streaming by ultrasound has a greater influence on reactions than shock waves generated by cavitation bubbles. In some cases, chemical effects of transient cavitation are revealed to have adverse influence on a reaction. Many biofuels systems are limited by their intrinsic characteristics that restrict the effect of ultrasound and cavitation on the reaction system.

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2.1 Introduction

Fast depletion of global fossil fuel reserves, sparking an almost four fold increase in international prices of crude oil has made energy security a daunting issue for developing economies. A related issue is that of climate change due to enormous rise in emissions of greenhouse gases from vehicular exhaust. Both of these issues have triggered immense research in alternate renewable energy sources (mainly the biofuels) in the past two decades. With growing economies, the energy demands in all sectors of a developing nation are rising fast, with major sectors being domestic, industry and agriculture. The main energy demand in these sectors is in two forms, viz. electricity and liquid transportation fuel. Numerous ways have been explored to fulfill these energy needs from renewable and carbon neutral bio-sources. The major routes for electricity are either biogas digestion or biomass gasification. Biogas digestion produces methane which could be used in engine generator sets. Biomass gasification produces a mixture of carbon monoxide and hydrogen, which also can be used in engine generator sets. Other alternate carbon neutral sources for electricity are solar (either photovoltaics or solar-thermal) and wind energy. As far as liquid transportation fuels are concerned, there are two main options, viz. alcoholic biofuels through fermentation and biodiesel. Alcoholic biofuels such as methanol, ethanol and butanol have been widely used for blending with gasoline (replacing the conventional methyl *t*-butyl ether, MTBE, as oxygenate). Biodiesel is essentially alkyl esters of fatty acids. These are produced by the process of esterification/transesterification of free fatty acids/triglycerides using short chain alcohols like methanol and ethanol. Like alcoholic biofuels, biodiesel can be blended with petro-diesel. Up to 20 % blends of diesel/biodiesel can be used in the vehicles without requiring modifications of engine.

Despite promise of these biofuels for mitigating the threats of energy security and climate change risk, large scale commercial production of these biofuels has been hampered by economic non-feasibility. For example, the total production cost of biodiesel is almost at par with petroleum-diesel. This is due to high cost of the feedstock (i.e. vegetable oil) coupled with large processing cost. For bio-diesel, use of low-cost non-edible oils like *Jatropha curcas* and *Karanja* offer a possible solution, but the processes based on these feedstocks have been largely unsuccessful due to non-availability of oil seeds for regular supply. There are three possible means of enhancing the economy of biodiesel production: (1) use of low-cost feedstock than non-edible oils such as microalgal lipids and animal fats which have high contents of free fatty acids (FFA); (2) use of efficient processing techniques that give high yield with faster kinetics for esterification (thus lowering the cost of recycle with simultaneous increase in the throughputs); (3) forward integration of the biodiesel process by conversion of byproducts such as glycerol to value-added products.

As far as alcoholic biofuels are concerned, the most popular fuel is ethanol, which is a major byproduct of the sugar industry. However, the substrate for ethanol, i.e. molasses, has numerous other outlets that fetch attractive revenue. This essentially increases the production cost of ethanol, as a result of which the producer is compelled to sell it for potable use, which fetches high price unless a sufficiently high minimum support price (MSP) is provided by Government for ethanol purchase by petroleum industry. Thus, the ethanol from sugar industry is largely unavailable for blending with gasoline. This necessitates exploration of alternate sources of cheaper ethanol. Fermentation of lignocellulosic biomass as substrate is a potential solution to this issue. The biomass available in the form of agro-residue or forest-residue or waste biomasses like invasive weeds and grasses have been extensively explored in lab-scale investigations for bioethanol production. The major bottleneck of bioalcohol production from this route is the high cost of biomass pretreatment. A simple, energy efficient and low-cost technology for effective biomass pretreatment can boost economy of alcoholic biofuels products several fold.

The efficiency of physical, chemical or biological process depends on the method of introduction of energy into the system to bring about the required transformation. Numerous new techniques have been invented in recent years that offer efficient and effective means of introduction of energy into the system, which gives higher yield as well as kinetics of desired transformation. One such technique is ultrasound irradiation or sonication. Ultrasound is essentially a longitudinal acoustic wave with frequency equal to or higher than 20 kHz—which is the upper limit of human hearing range. The propagation of ultrasound gives sinusoidal variation in the static pressure in the liquid medium. This phenomenon gives rise to cavitation in the medium. Cavitation can be defined as nucleation, volumetric oscillations and implosive collapse of tiny gas or vapor bubbles driven by ultrasound wave. Transient cavitation causes extreme energy concentration in the medium at an incredibly small temporal (~ 50 ns) and spatial scale (~ 100 nm) [1]. The transient implosive collapse of the bubble is adiabatic and the temperature and pressure inside the bubble reaches extremely high ($\sim 5,000$ K and ~ 50 MPa) [2, 3]. Transient cavitation has both physical and chemical effects on the reaction system. The physical effect is generation of intense local convection in the medium that enhances the mass transfer characteristics of the system. The chemical effect includes generation of highly reactive radicals inside the cavitation bubble at the moment of transient collapse, when the temperature and pressure in the bubble reach extrema. The radicals generated inside the bubble get released into the medium with fragmentation of the bubble where they can induce/accelerate chemical reactions. This is the well known sonochemical effect. Use of ultrasound for intensification of synthesis of biofuels has been attempted by many researchers and a voluminous literature (more than 300 papers) has been published in this area in the past few years. An excellent and comprehensive review of this literature has been recently published by Luo et al. [4]. Ultrasound has mainly been applied for the pretreatment of biomass (delignification/acid hydrolysis), enzymatic hydrolysis of pretreated biomass (or saccharification), fermentation of the hydrolyzates from acid/enzymatic hydrolysis,

microalgal lipid extraction, biodiesel synthesis and biogas digestion. Literature published in these area reports beneficial effects of ultrasound and cavitation on the process in terms of higher yield, faster kinetics, reduction in the number of process steps, use of cruder chemicals and substrates etc. However, very little effort has been dedicated to deduce the exact physical mechanism underlying the observed enhancement. The relative contribution of physical and chemical effects towards enhancement has not been discerned. For achieving effective design and scale-up of ultrasound based biofuels synthesis, the establishing exact physical mechanism of the ultrasound-induced enhancement is crucial.

In this chapter, critical analysis of our research in this area is given as applied to different biofuels systems. Review of general literature published in the area of ultrasound assisted biofuels synthesis is beyond the scope of this chapter. The focus of this chapter is to bring together all results of our research in linking the chemistry of biofuels synthesis with the physics of ultrasound and cavitation. Biofuel systems that are treated in this chapter are: (1) biomass pretreatment and hydrolysis, (2) biodiesel synthesis with homogeneous/heterogeneous acid/alkali catalyst, (3) microalgal lipid extraction, (4) bioethanol synthesis from lignocellulosic biomass with either separate hydrolysis and fermentation or simultaneous saccharification and fermentation and (5) bioconversion of crude glycerol from biodiesel industry to value-added products. Finally, a coherent mechanistic picture of ultrasound enhanced biofuels synthesis is proposed that gives research directions.

2.2 Physics of Ultrasound and Cavitation: A Brief Overview

Before proceeding to discussions on effects of ultrasound and cavitation on different biofuels systems mentioned in previous section, we briefly ponder over some basic physical aspects of ultrasound and cavitation. Greater details on this subject can be found in standard textbooks and monographs [5–12] and popular reviews [13–18].

2.2.1 Ultrasound Wave Phenomenon

Sound wave passes through a compressible medium, such as air and water, in the form of a longitudinal wave comprising of alternate compression and rarefaction phases. The pressure as well as density of the medium undergoes periodic variation with passage of the wave. The fluid elements in the medium undergo an oscillatory motion around a mean position. The sound wave is characterized on the basis of its frequency, velocity and pressure amplitude. Some basic relations between ultrasound frequency (f), velocity (c), pressure amplitude (P_A) oscillatory velocity of fluid elements (u), density of the medium (ρ), and the acoustic intensity

(I) are as follows: $u = 2\pi fa$ (where a is the amplitude of oscillation); $P_A = u\rho c$; $I = P_A^2/\rho c = 2\pi^2 f^2 a^2 \rho c$ [5, 6]. During its passage through the medium, the sound wave suffers from attenuation due to energy loss through several mechanisms like frictional (or viscous) loss, thermal loss and acoustic damping due to bubbles. The momentum of the wave is absorbed by the medium due to finite viscosity and this loss is manifested in terms of unidirectional circulatory currents set up in the medium (known as acoustic streaming). Bubbles present in the medium scatter the ultrasound waves causing severe attenuation. Presence of gas bubbles in the liquid also alters the compressibility of the medium, as a result of which the speed of sound in the medium reduces. The properties of the sound wave are also a function of the static pressure in the medium. As far as sound wave propagation in liquids is concerned, the static pressure in the medium is of insignificant importance, as the liquid properties are relatively insensitive to static pressures of moderate values. Thus, the properties of sound wave propagating in a liquid medium do not alter with static pressure of the medium for moderate rise in pressure levels.

2.2.2 Cavitation Bubble Dynamics

Cavitation is generally known to be a fluid transportation problem that damages the transport machineries. However, recent research has proven that controlled cavitation is a highly effective tool for intensification of physical and chemical processes. As noted earlier, the principal cause behind cavitation, which is nucleation, growth, oscillations and transient collapse of small gas bubbles due to pressure variation or in general, energy dissipation in the system. On the basis of this criterion, cavitation can be categorized as: *Acoustic cavitation*—which results due to pressure variation generated due to passage of an acoustic wave, and *Hydrodynamic cavitation*—which results due to pressure variation in the liquid flow due to change in the flow geometry. Theoretically, cavitation refers to creation of voids in the liquid medium by overcoming the Laplace pressure ($2\sigma/R$), which would require extremely high acoustic pressure amplitudes exceeding ~100 MPa. Practically, actual cavitation occurs at low pressure amplitudes that are attributed to phenomenon of nucleation. Nucleation occurs due to presence of solid particles or tiny free-floating bubbles present in the liquid that act as nuclei. Another source of nuclei is the gas pockets trapped in the crevices of the solid boundaries in the liquid medium. These gas pockets can grow in response to reduction in ambient pressure with passage of acoustic wave [19].

2.2.3 Radial Motion of Cavitation Bubbles

The periodic pressure variation caused by propagation of ultrasound wave gives rise to volume oscillations of cavitation bubbles. The amplitude of the volume

oscillations of the cavitation bubbles is a function of amplitude of the acoustic wave. For relatively small acoustic pressure amplitudes, the volume oscillations of the bubble are small-driven mainly by the pressure forces, and essentially in phase with the acoustic wave. For larger pressure amplitudes (typically greater than static pressure in the medium), the volumetric oscillations of the cavitation bubble become non-linear—comprising of an initial explosive growth followed by a transient collapse and few after-bounces. In this case, the volume oscillations (or radial motion) of the bubble are governed by pressure as well as inertial forces [20]. The model for radial motion of cavitation bubbles has been a subject of investigation for more than 100 years. The first-ever mathematical analysis of an empty cavity collapsing under constant static pressure was given by Rayleigh [21]. This analysis was improved in later years by several researchers to include the effects of surface tension and viscosity of liquid. Presence of non-condensable gas and solvent vapor inside the bubble was also accounted for. The popular Rayleigh–Plesset–Noltingk–Neppiras–Poritsky [22–24] equation for radial motion of bubble is as follows (Eq. 2.1):

$$R \frac{d^2 R}{dt^2} + \frac{3}{2} \left(\frac{dR}{dt} \right)^2 = \frac{1}{\rho} \left[\left(P_o + \frac{2\sigma}{R_o} - P_v \right) \left(\frac{R_o}{R} \right)^{3\gamma} + P_v - \frac{2\sigma}{R} - \frac{4\mu}{R} \frac{dR}{dt} - (P_o + P(t)) \right] \quad (2.1)$$

The above equation did not account for liquid compressibility, which becomes a dominant factor as the bubble wall velocity (dR/dt) becomes closer or even exceeds the sonic velocity in the medium. Later research in this area addressed this facet of bubble dynamics. The first model for cavitation bubble dynamics accounting for liquid compressibility effect was proposed by Gilmore [25] using Kirkwood-Bethe hypothesis [26] and Tait equation of state for liquid medium. Major developments occurred in this area during the subsequent years by Keller and Kolodoner [27], Keller and Miksis [28] and Prosperetti and Lezzi [29] have resulted in more rigorous forms of models for radial motion of cavitation bubbles. Two most popular equations for cavitation bubble dynamics among scientific community in bubble dynamics and sonoluminescence are:

1. Keller and Miksis equation [28, 30]:

$$\left(1 - \frac{\dot{R}}{c} \right) R \ddot{R} + \left(1 - \frac{3\dot{R}}{c} \right) \frac{3}{2} \dot{R}^2 = \frac{1}{\rho} \left(1 + \frac{\dot{R}}{c} \right) [p_g - P_o - P(t)] + \frac{\dot{R}}{\rho c} \frac{dp_g}{dt} - 4\nu \frac{\dot{R}}{R} - \frac{2\sigma}{\rho R} \quad (2.2)$$

In this equation the term $d^2(R^2\dot{R})/dt^2$ is calculated using Rayleigh–Plesset equation itself for the condition $\dot{R}/c \sim 1$, when the sound radiation by the bubble becomes important.

2. Another important variant of the bubble dynamics equation is the model proposed by Lofstedt et al. [31] and Barber et al. [32], in which all prefactors in the parantheses containing $\dot{R}/c$ are deleted. This leads to the equation:

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{1}{\rho}[p_g - P_o - P(t)] + \frac{\dot{R}}{\rho c} \frac{dp_g}{dt} - 4v\frac{\dot{R}}{R} - \frac{2\sigma}{\rho R} \quad (2.3)$$

2.2.4 Modeling of the Sonochemical and Sonophysical Effects

The passage of ultrasound wave through the medium gives rise to sinusoidal pressure variation in the medium. The cavitation bubbles grow from the nuclei in the medium during the rarefaction half cycle of ultrasound, when the pressure in the medium falls sufficiently below the ambient or static pressure. If the pressure amplitude of the ultrasound wave is sufficiently high, the bubble undergoes an explosive growth to several times its original size in the rarefaction half cycle of ultrasound. This expansion is accompanied by large evaporation of water at the bubble interface. The vapor molecules diffuse towards the core of the bubble after evaporation into the bubble. The vapor transport in the bubble is a crucial aspect of the cavitation bubble dynamics. This matter has been treated by numerous authors with different approaches [13, 33–41]. A review of literature treating vapor transport across bubble interface during radial motion and the entrapment of vapor in the bubble during transient collapse has been provided in our earlier paper [42].

The general treatment of the vapor transport and entrapment in the cavitation bubble was given by Storey and Szeri [43] in a landmark paper published in 2000. Storey and Szeri coupled the Navier–Stokes equations for gas mixtures in the bubble to the reaction mechanism between species in the bubble. The transport properties (thermal and mass diffusion and viscosity) were calculated from equations based on Chapman–Enskog theory and the equation of state was Redlich–Kwong–Soave type. Storey and Szeri [43] showed that in the compression phase of radial bubble motion, counter diffusion of the vapor molecules occurs with condensation at the bubble wall. The rate of transport of vapor molecules is proportional to the difference between partial pressure of liquid in the bubble and the saturation (or vapor) pressure at the bubble interface. However, not all of the vapor molecules that approach the bubble interface stick to it, giving rise to non-equilibrium phase change. The fraction of vapor molecules that stick to the bubble interface is the accommodation coefficient. The lower the value of this parameter, the greater the resistance to condensation and the higher the amount of vapor entrapped. The principal result of the study of Storey and Szeri was that water vapor transport in the bubble is a two-step process, i.e. diffusion to the bubble wall and condensation at the wall. Thus, it is influenced by two time scales, viz. time scale of diffusion (t_{dif}) and time scale of condensation (t_{cond}) [44], and their magnitudes relative

to the time scale of bubble dynamics, t_{osc} . In the initial phase of bubble collapse $t_{\text{osc}} \gg t_{\text{diff}}, t_{\text{cond}}$, due to which the phase change at the bubble interface is in equilibrium, and the concentration of vapor molecules at the bubble interface is essentially same as that in the bubble core. As the bubble wall acceleration increases during collapse, the time scales of bubbles dynamics and vapor diffusion becomes equal. At this stage, the rate of reduction of vapor molecules in the central region of the bubble is less than that at the bubble wall. With further acceleration of the bubble wall, $t_{\text{osc}} \ll t_{\text{diff}}$ condition is reached, and the vapor molecules have insufficient time to diffuse to the bubble wall, which results in a fixed and uneven distribution of vapor molecules in the bubble. At this condition, the bubble composition is “frozen” and the vapor present inside the bubble is essentially “trapped” in the bubble.

Another mechanism which traps vapor molecules inside the bubble is the non-equilibrium phase change at the bubble wall. In the final moments of bubble collapse, when $t_{\text{osc}} \ll t_{\text{cond}}$, the condensation or phase change at the bubble wall is non-equilibrium in that not all vapor molecules that approach the bubble wall can escape the bubble by undergoing phase change, and get trapped in the bubble. The exact mechanism by which water vapor gets trapped in the bubble is determined by relative magnitudes of t_{osc} , t_{cond} and t_{diff} . When the bubble dynamics time scale is smaller than either diffusion or condensation time scale, it leads to entrapment of the vapor. Storey and Szeri [43] showed that the condition $t_{\text{osc}} \ll t_{\text{diff}}$ is reached well before the condition of $t_{\text{osc}} \ll t_{\text{cond}}$. Thus, the contribution to vapor entrapment from diffusion mechanism is more than the condensation mechanism or in other words, vapor transport in the bubble is a diffusion limited process. The entrapped vapor and gas molecules in the bubble are subjected to extreme conditions generated during transient collapse due to which they undergo thermal dissociation to several chemical species—some of which are radical species which induce the sonochemical effect.

In view of the results of Storey and Szeri [43, 45], Toegel et al. [46] developed a simple diffusion limited model using boundary layer approximation, which has become immensely popular among the sonochemical community. This model, based on ordinary differential equations, has distinct merits of being simple yet physically realistic. This model has been validated against the full partial differential equation (PDE) model of Storey and Szeri [43, 45]. This model does not take into account the rectified diffusion of non-condensable gas across the bubble during radial motion, as the time scale of this diffusion, approximated by ratio R_0^2/D , is of the order of milliseconds (100 ms for typical values of $R_0 \sim 10 \mu\text{m}$ and $D = 10^{-9} \text{ m}^2/\text{s}$), while the bubble motion time scale is of the order of microseconds (50 μs for 20 kHz). As a result of large difference in the two time scales, practically no diffusion of gas occurs across bubble interface for the radial motion of few hundreds of acoustic cycles, and hence, the approximation of neglecting gas diffusion is good [47]. Another important assumption made while estimation of the sonochemical effect is that of prevalence of chemical equilibrium in the bubble all through radial motion. This assumption is again based on the relative time scales of reactions occurring inside the bubble and the timescale of bubble

dynamics. As the temperature and the pressure in the bubble at the point of maximum compression is extreme ($\sim 5,000$ K and ~ 50 MPa), and also that the concentration of different chemical species is very high due to extremely small volume. The rates of various reactions occurring between these species are also very high. As a result, chemical equilibrium prevails in bubbles all along during the radial motion [14, 42].

The essential equations and thermodynamic data of the diffusion limited ordinary differential equation (ODE) model are given in Tables 2.1 and 2.2 [48]. The main components of this model are: (1) Keller-Miksis equation for radial motion of cavitation bubbles, (2) Equation for the diffusive flux of solvent vapor through the bubble wall, (3) Equation for heat conduction across bubble wall and (4) Overall energy balance treating the cavitation bubble as an open system. The transport parameters for the heat and mass transfer are determined using Chapman–Enskog theory with Lennard–Jones 12–6 potential at the bulk temperature of the liquid [49–52]. The thermal and diffusive penetration depths are estimated using dimensional analysis from the radial motion of cavitation bubbles assuming that the condensation of vapor molecules at bubble interface is fast enough to maintain equilibrium. Thus the instantaneous diffusive penetration depth for mass transfer is given by Eq. 2.4:

$$l_{diff} = \sqrt{D_{ij}t_{osc}} \quad (2.4)$$

where D_{ij} is the binary diffusion coefficient and t_{osc} is the time scale of bubble oscillation taken as $R/|dR/dt|$. At the instance of maximum compression or minimum radius, the bubble wall velocity $|dR/dt| = 0$, and the above equation has a singularity. However, at the instance of minimum radius, the bubble is essentially a stagnant sphere, and the mass transfer is a purely diffusional process. Using the series solution for mass transfer through sphere [53], the upper limit for the diffusive penetration depth is found to be R/π . Thus, the mass diffusive penetration depth is given by Eq. 2.5:

$$l_{diff} = \min\left(R/\pi, \sqrt{RD_{ij}/|dR/dt|}\right) \quad (2.5)$$

Similar analysis can also be given for thermal diffusion, and the thermal diffusive length is given by Eq. 2.6:

$$l_{th} = \min\left(R/\pi, \sqrt{R\kappa/|dR/dt|}\right) \quad (2.6)$$

2.2.5 Numerical Solution

The set of 4 simultaneous ODEs in Table 2.1 can be solved using Range–Kutta 4th order–5th order adaptive step size method [54]. The cavitation bubble reaches extremely energetic and highly unstable state at the instance of maximum compression (or minimum radius) and may collapse. The word “collapse” essentially

Table 2.1 **a** The diffusion-limited model for the radial motion of cavitation bubble. **b** Thermodynamic properties of various species

Model component	Equation	Initial value
1. Radial motion of the cavitation bubble	$\left(1 - \frac{dR/dt}{c}\right) R \frac{d^2 R}{dt^2} + \frac{3}{2} \left(1 - \frac{dR/dt}{3c}\right) \left(\frac{dR}{dt}\right)^2$ $= \frac{1}{\rho_L} \left(1 + \frac{dR/dt}{c}\right) (P_i - P_t) + \frac{R}{\rho_L c} \frac{dP_i}{dt} - 4\nu \frac{dR/dt}{R} - \frac{2\sigma}{\rho_L R}$	At $t = 0$, $R = R_0$, $dR/dt = 0$
2. Diffusive flux of solvent (methanol) molecules	Internal pressure in the bubble: $P_i = \frac{N_{s,i}(t) kT}{4\pi(R^3(t) - R_0^3)/3}$ Pressure in bulk liquid medium: $P_t = P_0 - P_A \sin(2\pi f t)$ $\frac{dN_{S,i}}{dt} = 4\pi R^2 D_S \left. \frac{\partial C_S}{\partial r} \right _{r=R} \approx 4\pi R^2 D_S \left(\frac{C_{S,R} - C_{S,i}}{l_{diff}} \right)$	At $t = 0$, $N_S = 0$
3. Heat conduction across bubble wall	Instantaneous diffusive penetration depth: $l_{diff} = \min\left(\sqrt{\frac{RD_S}{ dR/dt }}, \frac{R}{\pi}\right)$ $\frac{dQ}{dt} = 4\pi R^2 \lambda \left. \frac{\partial T}{\partial r} \right _{r=R} \approx 4\pi R^2 \lambda \left(\frac{T_0 - T}{l_{th}} \right)$ Thermal diffusion length: $l_{th} = \min\left(\sqrt{\frac{R\kappa}{ dR/dt }}, \frac{R}{\pi}\right)$	At $t = 0$, $Q = 0$
4. Overall energy balance	$C_{V,mix} dT/dt = dQ/dt - P_t dV/dt + (h_S - U_S) dN_S/dt$ Mixture heat capacity: $C_{V,mix} = \sum C_{V,i} N_i$ ($i = N_2/O_2/Solvent$) Molecular properties of solvent: Enthalpy: $h = \left(1 + \frac{f_i}{2}\right) kT_o$ Internal energy: $U_S = N_S kT \left(3 + \sum_{i=1}^3 \frac{\theta_i/T}{\exp(\theta_i/T) - 1}\right)$ Heat capacity of various species ($i = N_2/O_2/Solvent$): $C_{V,i} = N_i k(f_i/2 + \sum (\theta_i/T)^2 \exp(\theta_i/T) / (\exp(\theta_i/T) - 1)^2)$	At $t = 0$, $T = T_0$

(continued)

Table 2.1 (continued)

Species	Degrees of freedom (translational + rotational) (f_i)	Lennard-Jones force constants		Characteristic vibrational temperatures θ (K)
		σ (10^{-10} m)	ϵ/k (K)	
N ₂	5	3.68	92	3,350
O ₂	5	3.43	113	2,273
CH ₃ OH	6	3.626	481.8	500.59, 1,674.41, 1,708.94, 1,854.22, 2,169.26, 2,356.26, 2,376.4, 2,392.22, 4,581.62, 4,649.23, 4,752.8, 5,923.74
Ar	3	3.42	124	—
H ₂ O	6	2.65	380	2,295, 5,255, 5,400

^a Data taken from Toegel [48], Hirschfelder et al. [49], Reid et al. [50], Davis [51], Condon and Odishaw [52]
Notations R —radius of the bubble; dR/dt —bubble wall velocity; c —velocity of sound in bulk liquid medium; ρ_L —density of the liquid; ν —kinematic viscosity of liquid; σ —surface tension of liquid; λ —thermal conductivity of bubble contents; κ —thermal diffusivity of bubble contents; θ —characteristic vibrational temperature(s) of the species; N_S —number of solvent molecules in the bubble; N_{N_2} —number of nitrogen molecules in the bubble; N_{O_2} —number of oxygen molecules in the bubble; t —time, D_S —diffusion coefficient of solvent vapor; C_S —concentration of solvent molecules in the bubble; $C_{S,R}$ —concentration of solvent molecules at the bubble wall or gas-liquid interface; Q —heat conducted across bubble wall; T —temperature of the bubble contents; T_σ —ambient (or bulk liquid medium) temperature; k —Boltzmann constant; h_S —molecular enthalpy of solvent; U_S —internal energy of solvent molecules; f_i —translational and rotational degrees of freedom; $C_{V,i}$ —heat capacity at constant volume for species i ; N_{tot} —total number of molecules (gas + vapor) in the bubble; h —van der Waal’s hard core radius; P_o —ambient (bulk) pressure in liquid; P_A —pressure amplitude of ultrasound wave; f —frequency of ultrasound wave

Table 2.2 a Summary of simulation results. Conditions at the first compression of the cavitation bubble. **b** Summary of simulation results. Equilibrium composition of the cavitation bubble contents in methanol at collapse conditions

a		
Parameter	Liquid medium	
	Methanol	Oil
$T_{\max}$ (K)	810	727
$P_{\max}$ (bar)	1,455	7.37
N_{MeOH}	3.88E+011	–
V_{turb} (m/s)	0.0205	0.00277
b		
Species	Equilibrium composition (mole fraction)	
CH ₄	7.3213E–01	
H ₂ O	2.2833E–01	
H ₂	2.0609E–02	
CO ₂	1.8203E–02	
C ₂ H ₆	3.1621E–04	
CO	4.1087E–04	
CH ₃ OH	1.5522E–07	
C ₂ H ₄	1.2378E–07	
CH ₃ COOH	2.8683E–08	
HCOOH	1.3946E–08	
H ₂ CO	2.4576E–08	

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Notations $T_{\max}$ —temperature peak reached in the bubble at the time of first collapse; $P_{\max}$ —pressure peak reached in the bubble at the time of first collapse; N_{MeOH} —number of methanol molecules trapped in the bubble at the instance of first collapse; V_{turb} —bulk liquid velocity (or the microturbulence velocity) generated by the cavitation bubbles

means fragmentation of the bubble [55, 56]. For conditions of maximum shape and flow instability, the cavitation bubble fragmentation can occur at the first compression after an initial expansion. Thus, for determination of the chemical composition of the contents of cavitation bubble using thermodynamic equilibrium approximation, the temperature and pressure inside the bubble can be taken at the instance of first compression.

2.2.6 Physical Effects of Cavitation Bubble

Ultrasound and cavitation render several physical effects on a reaction system. The main manifestation of all of these results is generation of intense micro-convection and micro-mixing in the reaction system. A brief description of all physical effects of ultrasound and cavitation is given below [9–12]:

Micro-streaming: This is essentially small amplitude oscillatory motion of fluid elements around a mean position, which is induced by propagation of ultrasound wave. The velocity of micro-turbulence is given as: $u = P_A / \rho C$, where P_A —pressure amplitude of acoustic wave, ρ is the density of the medium and C is the velocity of sound in the medium. For a typical ultrasound wave with pressure amplitude of 120 kPa in water ($\rho = 1,000 \text{ kg/m}^3$, $C = 1,500 \text{ m/s}$), the micro-streaming velocity = 0.08 m/s.

Acoustic streaming: During propagation of ultrasound wave, the momentum of the wave is absorbed by the medium due to finite viscosity. This results in setting up of low velocity unidirectional currents of the fluid known as acoustic streaming [57, 58]. The phenomenon of acoustic streaming also occurs in the vicinity of solid boundaries in the medium, where the oscillatory motion of fluid elements is obstructed and results in setting up of unidirectional current parallel to the boundary.

Microturbulence: The oscillatory motion of fluid induced by an oscillatory bubble in its vicinity is called microturbulence. This phenomenon is explained as follows: in the expansion phase of radial motion of the cavitation bubble, the liquid is displaced away from bubble interface. During the collapse phase the liquid is pulled towards the bubble as it fills the vacuum created in the liquid with size reduction of bubble. The mean velocity of microturbulence depends on the amplitude of bubble oscillation. However, it was noted that phenomenon of microturbulence is restricted only in the region in close vicinity of the bubble. The microturbulence velocity diminishes very rapidly away from the bubble.

Acoustic (or shock) waves: During the compression phase of radial motion, as the bubble contracts void space is created in the liquid, and the fluid element spherically converge (or essentially “gush”) in this void space and work is done on the bubble. For a cavitation bubble containing non-condensable gas such as air, the adiabatic compression results in rapid rise of pressure inside the bubble. At the point of minimum radius (or maximum compression), the bubble wall comes to a sudden halt. At this instance, the fluid elements converging towards the bubble are reflected back from the interface. This reflection creates a high pressure shock wave that propagates through the medium. The pressure exerted by the non-condensable gas inside the bubble causes rebound of the bubble.

Microjets: During radial motion driven by ultrasound wave, the cavitation bubble maintains spherical geometry as long as the motion of liquid in its vicinity is symmetric and uniform, and thus there are no pressure gradients. If the bubble is located close to a phase boundary, either solid–liquid, gas–liquid or liquid–liquid, the motion of liquid in its vicinity is hindered, resulting in development of pressure gradient around it. This non-uniformity of pressure results in the loss of spherical geometry of the bubble. Numerous authors [59–67] have investigated this phenomenon in the past three decades—either theoretically (numerical simulations) or experimentally (high speed photography). During the asymmetric radial motion, the portion of bubble exposed to higher pressure collapses faster than rest of the bubble, which gives rise to the formation of a high speed liquid jet. However, the direction of this jet depends on the characteristics of the solid

boundary. Rigid boundaries such as metal surfaces are characterized by the boundary condition: $\nabla \cdot \phi = 0$, where ϕ is velocity potential at the boundary, while free boundaries (or pressure release boundaries such as gas–liquid interface) are characterized by condition $\phi = 0$. For a rigid boundary, the microjet is directed towards the boundary, while for a free boundary, the microjet is directed away from the boundary. The velocity of these microjets has been estimated in the range of 120–150 m/s [59–67]. In case of rigid boundaries, these jets can cause severe damage at the point of impact and can erode the surface.

2.3 Discerning the Physical Mechanism of an Ultrasonic Process

2.3.1 Discriminating Between Physical and Chemical Effects

The bubble dynamics model described earlier (Sect. 2.2.4) offers an efficient tool to estimate the physical and chemical effects of cavitation, and also to discriminate between them. Sonophysical and sonochemical effects mentioned earlier are induced by transient cavitation. The radial bubble motion is governed by two forces: viz. pressure force and inertial force. For transient cavitation to occur, the pressure amplitude of the ultrasound wave driving has to exceed a minimum level or limit, known as transient cavitation threshold. For acoustic pressure amplitudes above this threshold value, the bulk pressure in the medium falls to sufficiently low values below the ambient pressure of 101.3 kPa in the rarefaction half cycle of the wave, and the radius of the cavitation bubble expands to more than double of its original size. Since the bubble motion is dominated by inertial force, the bubble keeps on expanding even after completion of rarefaction half period [13, 20]. The ensuing collapse phase is also dominated by inertial force. The spherical convergence of fluid elements imparts high kinetic energy to the bubble causing a transient collapse that generates extreme condition of temperature and pressure as mentioned earlier. The transient cavitation threshold is mainly a function of the frequency of the ultrasound wave and the initial size of the cavitation bubble [15]. However, if the size of the cavitation bubble is far smaller than the resonant size corresponding to the frequency, the transient cavitation threshold is essentially same as the static pressure in the medium [15]. This approximation applies to bubbles in the size range of 1–10 μm and frequencies in the range of 20–100 kHz, which is the typical range of power ultrasound used in physical and chemical processing.

Discriminating between the physical and chemical effects of ultrasound and cavitation would essentially mean elimination of the transient cavitation, while leaving the ultrasound wave phenomenon unaltered. A simple technique to achieve this is to raise the static pressure of the medium, so that fall in the bulk pressure in the medium during rarefaction half cycle of the acoustic wave is reduced. The acoustic pressure amplitudes in commercial ultrasound equipment rarely exceed 200 kPa. Therefore, raising the static pressure of the medium to even moderate values of 400–500 kPa can help achieve complete elimination of the transient

cavitation [68] and the associated effects such as generation of radicals and shock-waves. However, since the liquid properties such as density, viscosity and surface tension remain practically same at 100 and 500 kPa, the ultrasound wave propagation is not influenced by elevated static pressure. Especially the phenomenon of strong micro-mixing induced by micro-streaming remains unchanged. Therefore, at elevated static pressure the ultrasonic system is essentially equivalent to mechanically stirred system, yet with mixing on micro-scale instead of bulk scale as in the case of conventional mechanical agitation.

We have extensively used the technique of elevated static pressure in our studies of different biofuels systems. The following sections of this chapter show application of elevated static pressure for many biofuel systems.

2.4 Mechanistic Insight into Ultrasound Enhanced Biofuels Processes

In this section, a summary of our studies in mechanistic investigations of different biofuels systems is given. The main approach in these studies has been to identify the exact role played by ultrasound and cavitation in the enhancement of process, and to identify and discriminate the contribution of physical and chemical effects of ultrasound and cavitation. Initially, we describe our major results and findings for different individual biofuels systems; and finally, we present a broad overview and analysis of these findings, which gives a cogent and coherent picture of the exact role of ultrasound and cavitation in the field of biofuels.

2.4.1 *Microalgal Lipid Extraction*

Microalgal route to biodiesel has been extensively investigated in the past one decade. The lipids produced by certain species of microalgae are potential feedstock for biodiesel that can be substituted for vegetable oil. Efficient extraction of these lipids is an important step in the biodiesel synthesis. Ranjan et al. [69] made a mechanistic assessment of this process. The relative contribution of two principal mechanisms of extraction of lipids, viz. cell disruption and diffusion across cell wall, to the overall lipid yield was determined. Three processes for extraction of lipids were assessed with three conventional methods, viz. Soxhlet extraction, Bligh and Dyer method and sonication. Two types of solvents were used for extraction, viz. n-hexane and mixture of chloroform and methanol. Sonication of the biomass mixture was carried out with both types of solvents. Simulations of cavitation bubble dynamics were carried out for both n-hexane and chloroform-methanol solvents. Microscopic analysis of the algal biomass after extraction was also done (Fig. 2.1). The trend in extent of lipid extraction was found as follows: Soxhlet extraction (n-hexane) $\approx$ sonication with n-hexane < Bligh and Dyer method with chloroform-methanol $\ll$ sonication with chloroform-methanol.

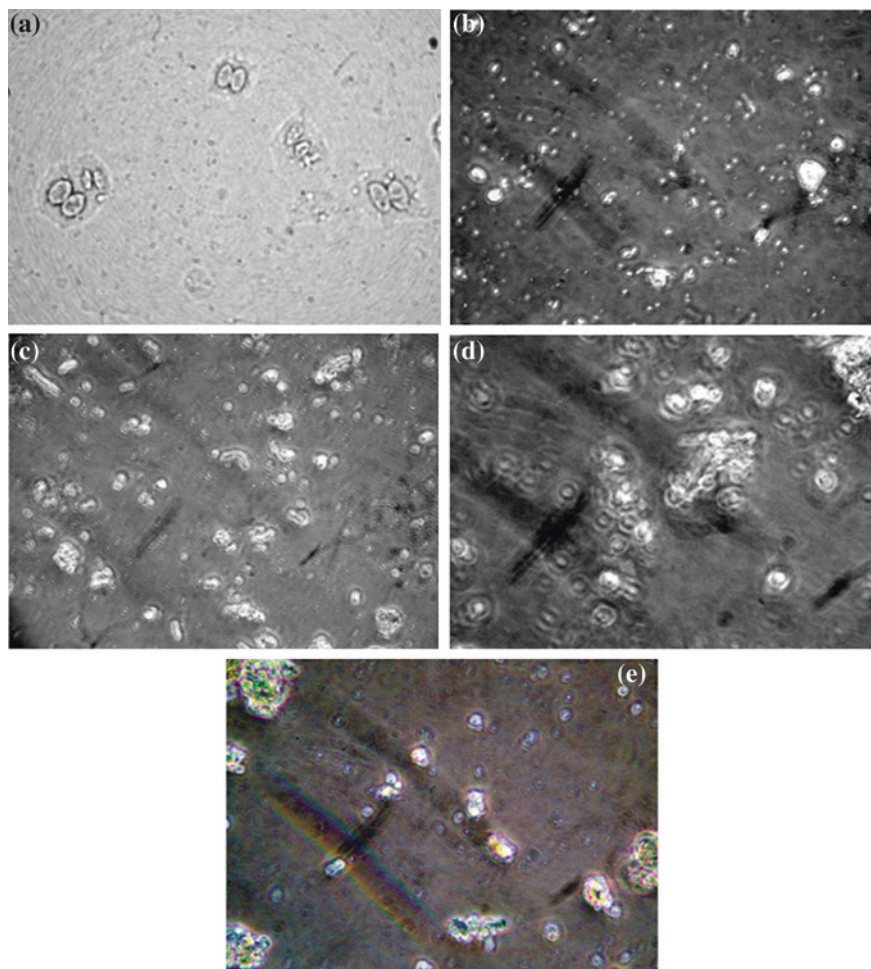
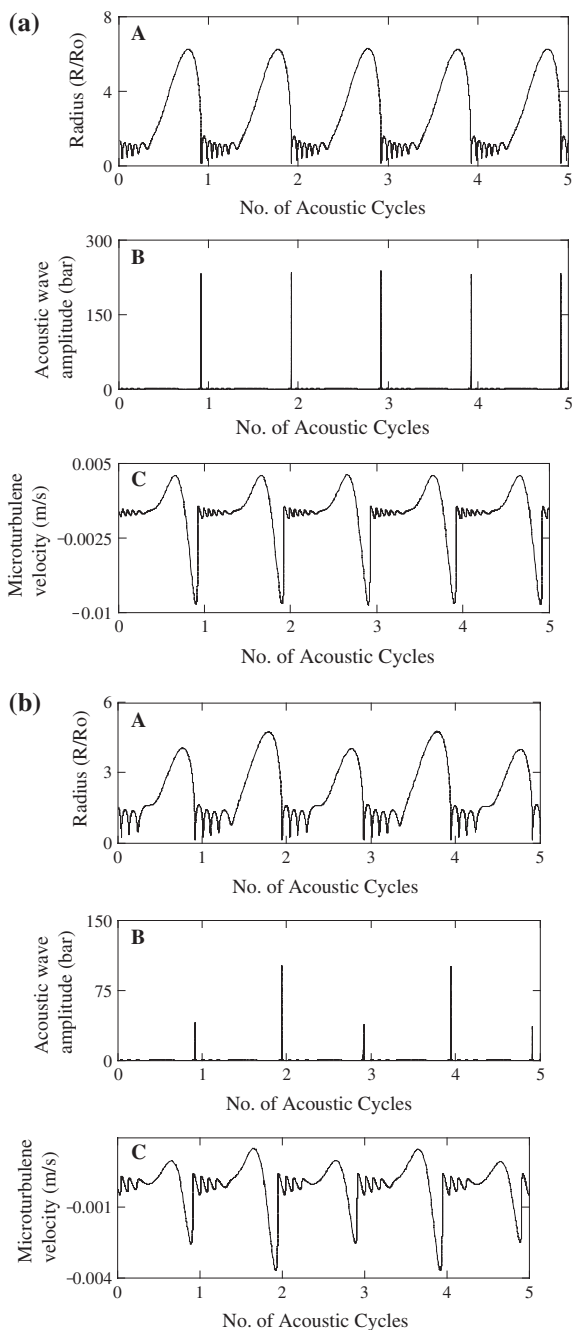


Fig. 2.1 Representative micrographs of the algal biomass before and after extraction of lipids with various techniques. **a** Original algal cells of *Scenedesmus* sp.; **b** biomass after extraction with soxhlet apparatus; **c** biomass after extraction with Bligh and Dyer method; **d** biomass after extraction using sonication with n-hexane as solvent; **e** biomass after extraction using sonication with chloroform-methane mixture as solvent. Reprinted with permission from [69], Copyright © 2010, American Chemical Society

The micrographs of algal biomass revealed no disruption of biomass with Soxhlet extraction (indicating diffusion as the only mechanism of lipid extraction; while Bligh and Dyer method as well as sonication indicated disruption of biomass indicating both cell disruption and diffusion as the possible mechanisms.

Simulations of cavitation bubble dynamics indicated microturbulence as well as shock waves of much higher magnitude for n-hexane as solvent than chloroform-methanol (Fig. 2.2a, b). It was an interesting anomaly that despite stronger

Fig. 2.2 a Simulations of the radial bubble motion and its physical effects in *n*-hexane. Time history of (A) normalized bubble radius (R/R_0); (B) acoustic waves emitted by bubble; (C) velocity of microturbulence generated by the bubble. Reprinted with permission from [69], Copyright © 2010, American Chemical Society. **b** Simulations of the radial bubble motion and its physical effects in chloroform-methanol. Time history of (A) normalized bubble radius (R/R_0); (B) acoustic waves emitted by bubble; c velocity of microturbulence generated by the bubble. Reprinted with permission from [69], Copyright © 2010, American Chemical Society



turbulence generated in n-hexane, extraction of lipids with mixture of chloroform-methanol as solvent was higher. These results brought out following mechanistic facts of ultrasound-assisted microalgal lipid extraction: (1) shock waves originating from transient cavitation are capable of disrupting microalgal cells causing rapid release of lipids. However, the extent of disruption depended on the probability of interaction of cells with cavitation bubbles. This probability would depend on the density of microalgal cells in the medium.

Due to rather dilute solution of microalgal biomass, the probability of cell-bubble interaction was low, and hence, complete disruption of biomass was not achieved. This phenomenon put limitations on the contribution of disruption mechanism to overall extraction of lipids, and thus, diffusion across cell wall was a major factor. (2) The extent of lipid extraction by process of convective diffusion (which is far slower than lipid extraction by cell disruption) depends on the intensity of bulk convection in the medium.

In case of sonication, the convection in the medium is generated by microstreaming and microturbulence. The second governing factor is the selectivity of solvents. The chloroform-methanol mixture, being polar in nature, will have much higher selectivity and partition coefficient than the non-polar hexane. Despite higher convection in n-hexane, greater extraction of lipids in chloroform-methanol mixture clearly indicated that solvent selectivity or partition coefficient is the dominant factor in lipid extraction than the intensity of convection in the medium. The role of ultrasound in the extraction process seemed to be more of physical nature in that intense convection generated by ultrasound and cavitation sweeps away lipids diffused out of cell wall from the liquid-microalgae interfacial region, thus maintaining a constant concentration gradient for the continuous diffusion of lipids from the cells.

2.4.2 Ultrasonic Synthesis of Biodiesel

Biodiesel, which essentially is alkyl esters of fatty acids, is synthesized by the esterification/transesterification reaction with either an acid or alkali catalyst. Our first investigation in ultrasound-assisted biodiesel synthesis aimed at discerning the individual contributions of physical and chemical effects of transient cavitation towards the transesterification reaction. Kalva et al. [70] conducted experiments in following categories to deduce the possible ultrasonic enhancement of transesterification: (1) no addition of external base catalyst so that the transesterification reaction would be initiated by methoxide radicals produced by reaction between OH radicals generated by transient cavitation and the methanol molecules; (2) addition of Fe^{2+} to methanol so that the Fenton reaction between Fe^{2+} and OH radicals generated by transient cavitation would result in in situ generation of OH^- ions, which would then react with methanol to generate methoxide ions for transesterification. No biodiesel was produced with these techniques showing that the influence of ultrasound on transesterification reaction system was determined to be of a physical nature. Simulations of cavitation bubble dynamics corroborated this conclusion.

Cavitation can occur both in the oil and methanol phase. Due to large vapor pressure of methanol, large evaporation of methanol molecules takes place inside the bubble. Accordingly, the peak temperature and pressure attained during at transient collapse is reduced. The radial motion of cavitation bubble in methanol and oil has been depicted in Figs. 2.3 and 2.4. The summary of the simulation results has been given in Table 2.2. Although thermal dissociation of methanol molecules occurs during collapse, the species resulting from this are molecular species such as CH_4 , H_2O , H_2 and CO_2 . No formation of radical species was seen. This result basically confirmed that intensification of transesterification reaction by ultrasound was due to emulsification effect, which generated enormous interfacial area between oil and methanol phases.

With these results, further experiments were carried out with external addition of the base catalyst and the alcohol to oil molar ratio was varied in the range of 6:1, 12:1, 16:1 and 24:1. Higher yields were obtained in all the experiments at ambient temperature, but quite interestingly, the biodiesel yield passed through a maximum for an alcohol to oil ratio of 12:1. An explanation for this result is given as follows. Although cavitation and ultrasound wave phenomenon occurs in both oil and methanol phase, the velocities of micro-streaming and microturbulence are far higher in methanol due to its viscosity being lower than oil. For molar ratio of 6:1, the methanol phase forms the minor fraction of the reaction mixture, as compared with the oil phase. Thus, the dispersion of methanol in oil phase decides the interfacial area for reaction. Due to high level of microturbulence generated by cavitation bubbles in methanol, the dispersion of methanol in oil phase is uniform. However, the production of methoxy (CH_3O^-) ions is limited due to smaller volume of methanol, which places a limit on biodiesel yield.

At a molar ratio of 12:1, the equilibrium of methoxide formation reaction shifts favorably towards CH_3O^- and higher concentration of CH_3O^- leads to faster reaction. Moreover, the volume of methanol is still smaller than the oil, making methanol as dispersed phase and oil as continuous phase. Due to stronger microturbulence and micro-streaming in methanol, the dispersion of methanol in oil is uniform, leading to high interfacial area. Combination of higher CH_3O^- concentration and high interfacial area leads to higher yield of biodiesel. As the molar ratio of alcohol to oil increases to 16:1, the volume of oil and methanol in the reaction mixture become comparable; and thus, interfacial area is determined by the dispersion of oil as well. Since the micro-streaming and microturbulence velocities in oil are very low, oil does not get dispersed properly in methanol, and hence, interfacial area reduces. At the highest molar ratio of 24:1, the problem of low dispersion of oil is even more pronounced leading to further reduction in interfacial area. Hence, the kinetics and yield of biodiesel reduces further. The study of Kalva et al. [70] clearly brought out the roles of physical and chemical effects of ultrasound and cavitation in transesterification reaction catalyzed by an alkali.

The experimental framework developed by Kalva et al. has been extended further to acid catalyzed transesterification process by Parker et al. [71]. Acid catalyzed ultrasonic transesterification revealed many interesting mechanistic features,

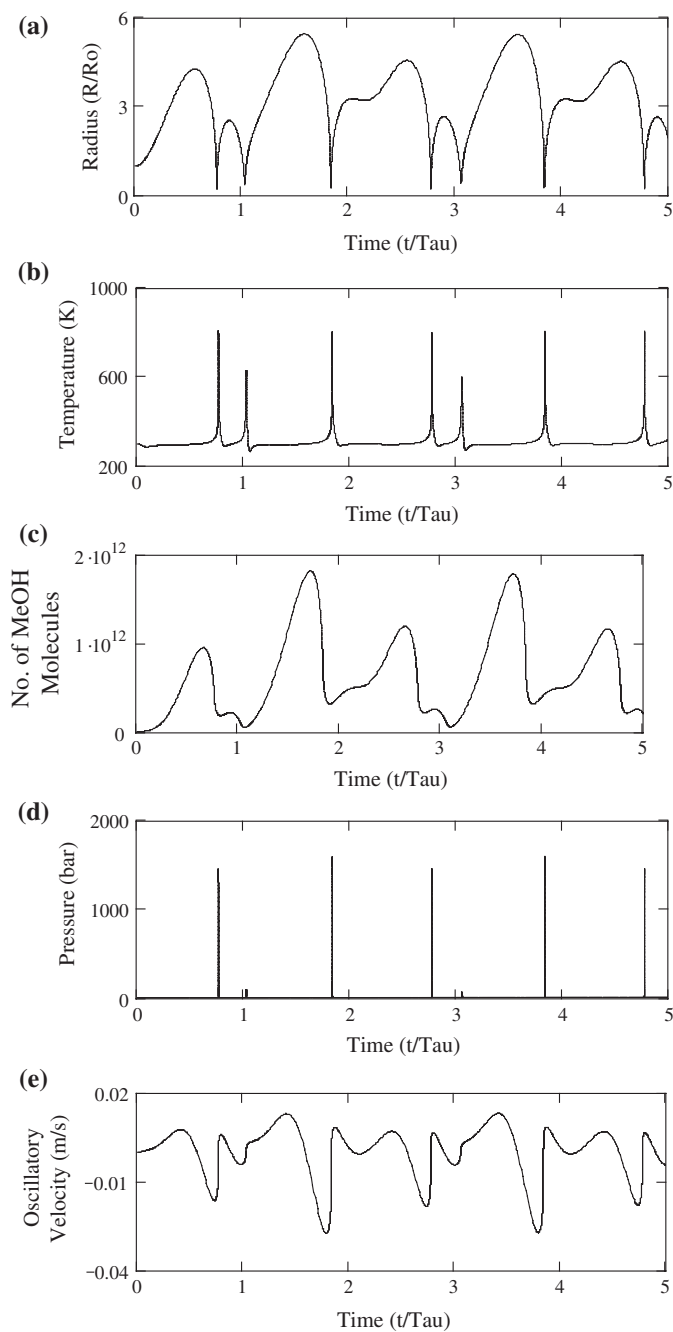


Fig. 2.3 Simulation results of radial motion of a 10 μm cavitation bubble in methanol medium. Reprinted with permission from [70], Copyright © 2009, American Chemical Society

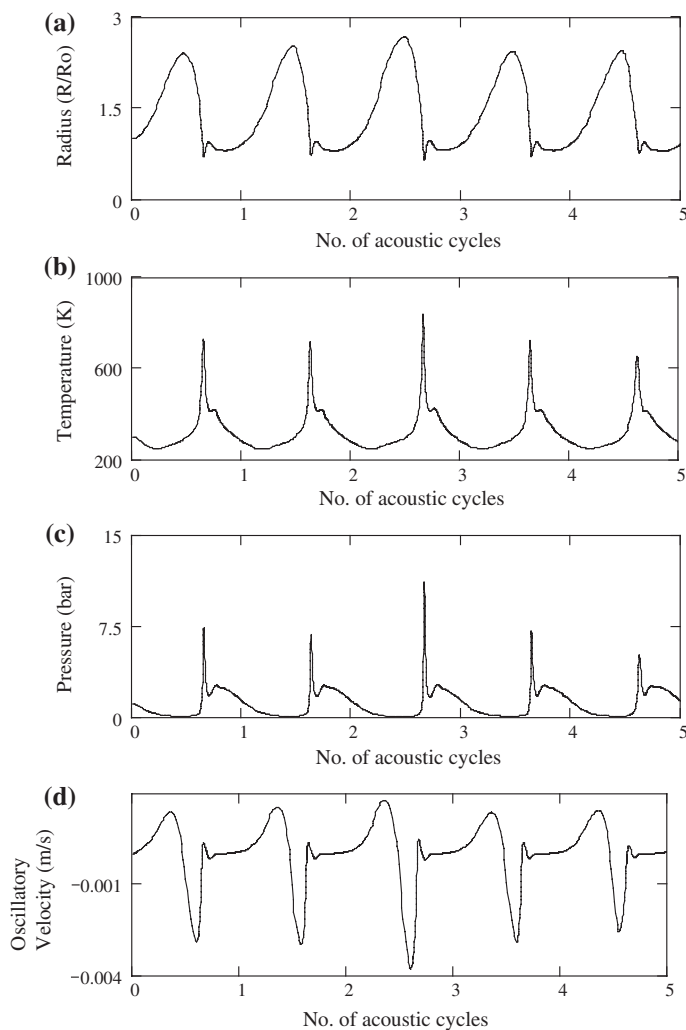
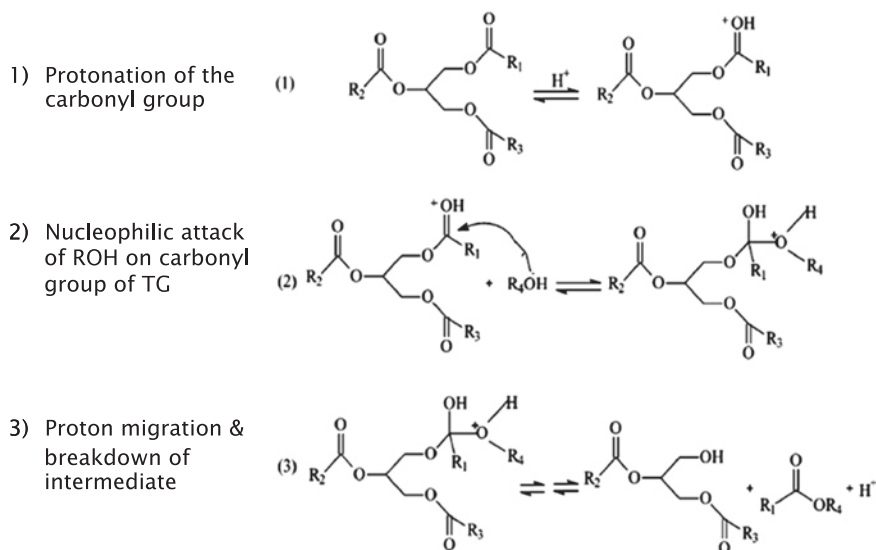


Fig. 2.4 Simulation results of radial motion of a 10 μm cavitation bubble in oil medium. Reprinted with permission from [70], Copyright © 2009, American Chemical Society

which were quite atypical of base catalyzed reaction. Compared to mechanically agitated systems, ultrasonic transesterification with acid catalyst showed several anomalies such as the occurrence of reaction at a low temperatures (15 °C), high reaction rate constants for alcohol ratio of 6:1 despite the high activation energy, and a minimum in reaction rate constant at temperatures in the range of 15–65 °C. These results, when correlated with simulation of cavitation bubble dynamics, revealed interesting physical mechanistic facts of acid-catalyzed transesterification.



Scheme 2.1 Chemical mechanism of acid catalyzed transesterification reaction

Before simulation can be discussed, it is important to note the basic difference in chemical mechanism of transesterification catalyzed by base [70] and acid [71]. Unlike alkoxide anion generated by reaction between alcohol and alkali catalyst in case of base-catalyzed transesterification; it is the direct protonation of triglycerides by acid catalyst that initiates the reaction (Scheme 2.1). Protonation of triglycerides generates electrophilic center on the carbonyl carbon making it susceptible to nucleophilic attack of methanol. Therefore, the rate controlling step for acid catalyzed transesterification is the probability of interaction between proton generated by acid catalyst that is in the methanol phase and the triglyceride that is in the organic phase. With increasing alcohol to oil molar ratio, the concentration of acid catalyst decreases, and so does the probability of interaction between proton and triglyceride—although the macroscopic equilibrium constant shift towards product. Reduction in the concentration of protons with increasing alcohol ratio causes reduction in macroscopic rate constant at any temperature. For the same reason, the highest rate constant and yield is obtained for an alcohol ratio of 6:1, as against 12:1 in case of base-catalyzed process. This result clearly indicates that intrinsic kinetics of acid catalyzed transesterification overwhelms the physical effect of emulsification and enhancement of interfacial area, which eliminate mass transfer effects. However, keeping the parameters for intrinsic kinetic constants the influence of physical effects of ultrasound and cavitation is evident from trends in kinetic constants and yield with temperature.

The numerical simulation of cavitation bubble dynamics in methanol (aqueous phase of reaction mixture) reveals that the intensity of the shock waves generated by cavitation bubble at 15 °C are much higher than those generated at 25 °C. Thus, greater emulsification is achieved at 15 °C resulting in greater interfacial area.

This physical effect overwhelms the intrinsic kinetics at lower temperature, and hence, higher rate constants are seen at 15 °C than at 25 °C. However, as the temperature of the reaction increases further to 45–65 °C the intrinsic kinetics dominates and higher rate constant than at 15 °C are obtained. These results have again demonstrated the physical or mechanistic features of ultrasonic biodiesel synthesis. Parkar et al. [71] also determined the activation energies for different alcohol to oil molar ratios. The least activation energy of 27.53 kJ/mol was obtained for molar ratio of 12:1. Despite the lowest activation energy (which would give the lowest specific rate constant at any temperature), the overall yield and kinetic constant was lower for the molar ratio of 12:1 at 15 °C.

Further mechanistic investigations in ultrasonic biodiesel synthesis were based on statistical design of experiments (DOE) that were coupled with simulation of cavitation bubble dynamics. The reaction systems studied in these investigations were: (1) biodiesel synthesis with heterogeneous base (CaO) catalyst [72]; (2) acid catalyzed (2 step) biodiesel synthesis of *Jatropha* oil; (3) heterogeneous base (CaO) catalysed biodiesel synthesis with *Jatropha curcus* oil; (4) single step ultrasonic and biodiesel synthesis from crude *Jatropha curcus* oil. We give below a brief description of the major results of these studies based on correlation with the simulation of cavitation bubble dynamics model.

1. In the first study, soybean oil was used as feedstock and Box–Behnken statistical design of experiments was employed to optimize the transesterification. The optimization parameters were temperature, alcohol to oil molar ratio and catalyst loading, with transesterification yield as the objective function. The optimum values of these parameters for the highest yield were identified through response surface methodology (RSM) using a quadratic model and analysis of variance (ANOVA). The response surface plots have been depicted in Fig. 2.5. The optimum values of the parameters were: Temperature = 62 °C, molar ratio = 10:1 and catalyst loading of 6 wt%. The activation energy was determined as 82.3 kJ/mol, which was higher than the value for homogenous catalyst (typically in the range of 20–30 kJ/mol). Analysis of experimental results vis-à-vis simulation of cavitation bubble dynamics revealed the mechanistic features of the process. The reaction system in the present case was three-phase heterogeneous, and hence, mass transfer resistance was more pronounced. The optimum temperature of the process was close to boiling point of methanol. Due to very large evaporation of methanol into the bubble, the transient collapse of the bubble was not much energetic. The peak temperature in the bubble reached ~700 K, which is not sufficient to generate radical species. The microturbulence induced by the bubble was accordingly less intense, and the contribution of micro-streaming to the overall convection in the medium was relatively much higher. The base catalyst CaO, being heterogeneous in nature, preferably stays in the aqueous (or methanol) phase. The methoxy ions in this case are generated by adsorption of methanol molecules on the catalyst surface. These methoxy ions are then transferred to organic phase at the interface between oil and methanol phase. Micro-streaming by ultrasound can enhance the rate of adsorption and enhance CH_3O^- production.

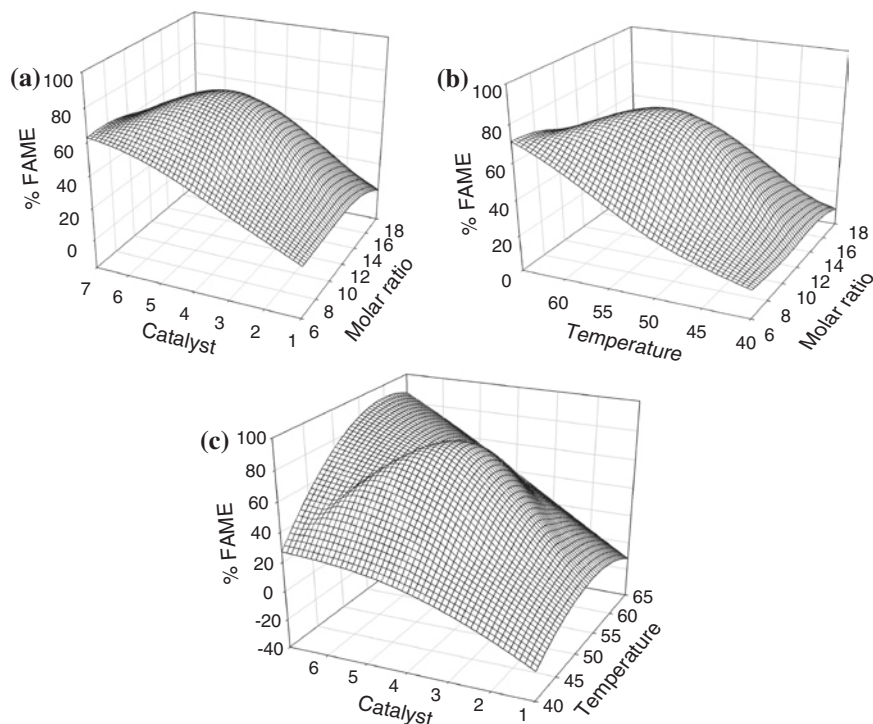


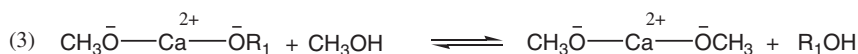
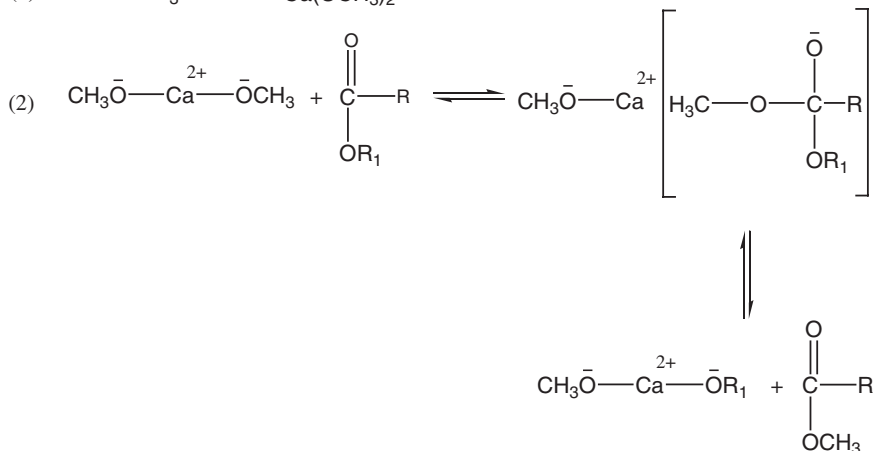
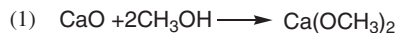
Fig. 2.5 Response surface plots for percentage of fatty acid methyl ester (FAME) yield as a function of reaction temperature, catalyst loading and methanol-to-oil molar ratio. Reprinted with permission from [72], Copyright © 2014, Elsevier

However, unlike the homogenous base where reaction at ambient temperature gave high yield of biodiesel; the optimum temperature in the case of heterogeneous catalyst was 62 °C. This essentially means that enhancement of mass transfer due to ultrasound does not overcome the intrinsic kinetic limitations of the process, that can be attributed to the high activation energy of the system. However, the optimum alcohol ratio of 10:1 is almost similar to that for the homogenous system (12:1). The explanation for this can be given along similar lines as that for homogenous system. The statistical model predicted strong interaction between effects of all optimization parameters on the FAME yield. The parameters of catalyst loading and molar ratio and temperature and molar ratio are related through the variation in convection level in the medium, which in turn related to cavitation bubble dynamics and ultrasound wave phenomena. The parameters of catalyst loading and temperature are related through intrinsic kinetics of the process. Some carbonate impurity in the catalyst could have also contributed to a reduction in the yield.

2. Choudhury et al. [73] have also done mechanistic investigations on acid catalyzed biodiesel synthesis from *Jatropha curcus* oil. This oil has much higher

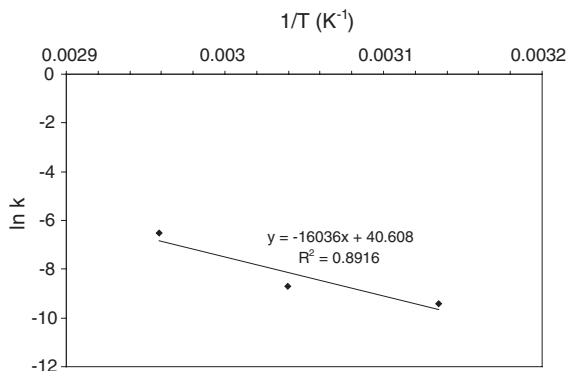
contents of free fatty acids than conventional refined oils. Therefore, the process was carried out in two stages, viz. esterification of free fatty acids followed by transesterification of triglycerides. Once again, a statistical design of experiments based on Box–Behnken method using response surface methodology was coupled with simulation of cavitation bubble dynamics. The acid catalyzed esterification was insensitive to ultrasound irradiation, while the beneficial effect of sonication on transesterification reaction was only through intense micro-mixing induced by ultrasound, as transient cavitation in methanol does not produce any radical species. Even at higher temperatures of 70 °C or 85 °C, and high catalyst concentration of 6 %w/w or 9 %w/w oil, the biodiesel yield was low for alcohol to oil molar ratio of 4:1. Low yield was attributed to low extent of emulsification that gives low interfacial area—as the transient cavitation in alcohol and not oil is responsible for emulsification effect. Reduced interfacial area between oil and methanol restricts the extent of protonation of carbonyl carbon of triglycerides. The biodiesel yield was also low at a temperature of 55 °C and an alcohol molar ratio of 10:1. The low yield was attributed to lower concentration of protons in aqueous phase at high alcohol ratios, due to which the probability of interaction between triglyceride and proton at interfacial area between phases is reduced. Raising of catalyst concentration to 9 wt% and temperature of 70 °C doubles this yield. The relative influence of mass transfer and intrinsic kinetics of the process is evident from these observations. The optimum set of process parameter as identified by the statistical design of experiments was alcohol to oil molar ratio = 7, catalyst concentration = 6 wt%, and temperature = 70 °C. The kinetics of the acid catalyzed transesterification was found to be much slower than base catalyzed process, which is attributed to basic difference in the chemical mechanism of acid and alkali catalyzed transesterification. The transesterification for acid catalyst is initiated by nucleophilic attack of methanol on the protonated carbonyl carbon of triglycerides. Since methanol is a poor nucleophile, its intrinsic reactivity is much less than the methoxide (CH_3O^-) ion, which initiates the transesterification in base catalyzed process. This is essentially manifested in slower kinetics of the reactions. These experimental trends clearly show that enhanced mass transfer with ultrasound is not sufficient to boost the overall kinetics of the process leading to higher biodiesel yield. Therefore, for high yield of transesterification process an overall optimization in terms of all parameters is necessary.

3. Choudhury et al. [74] have extended the above theme of two-stage biodiesel synthesis from *Jatropha curcus* oil with acid catalyst in the transesterification step replaced by solid base catalyst. The chemical mechanism of CaO catalyzed transesterification reaction is depicted in Scheme 2.2. The results of experiments using ultrasound were compared with mechanically agitated system. The statistical design of experiments yielded optimum parameters as: alcohol to oil molar ratio ~11, catalyst concentration = 5.5 wt% and temperature = 64 °C. The XRD analysis of catalyst revealed formation of calcium methoxide $\text{Ca}(\text{OMe})_2$ phase, which is the active catalyst for transesterification



Scheme 2.2 Proposed chemical mechanism of calcium oxide catalyzed transesterification reaction. Reprinted with permission from [72], Copyright © 2014, Elsevier

Fig. 2.6 Arrhenius plot of $\ln(k)$ versus $1/T$ for transesterification reaction considering 3rd order reaction kinetics (with respect to triglyceride) for optimum conditions of methanol to oil molar ratio (11:1) and catalyst concentration (5.5 wt%) as determined by statistical analysis. Reprinted with permission from [74], Copyright © 2014, Elsevier

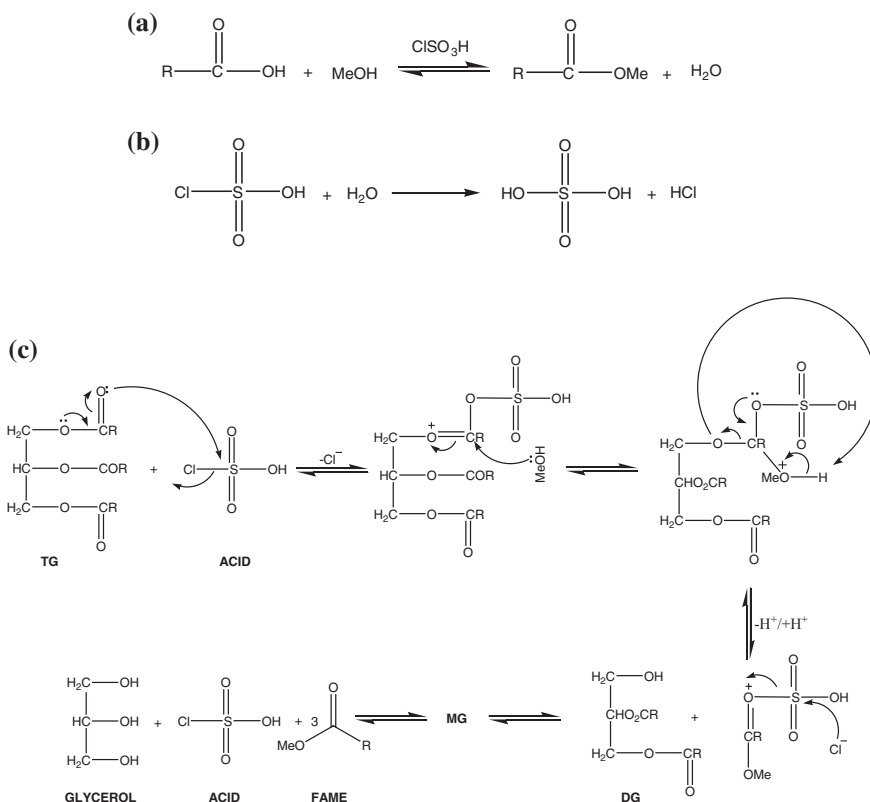


reaction. The activation energy of the ultrasonic process was found to be 133.5 kJ/mol, and this is attributed to 3 phase heterogeneity of the system. As compared to the previous study of Choudhury et al. [72] using refined soybean oil as a feedstock, which showed an activation energy of 82.3 kJ/mol (refer to the Arrhenius plot shown in Fig. 2.6), ~50 % higher activation energy for *Jatropha* could also be attributed to crudeness of oil. The impurities in the oil could poison the catalyst by adsorbing over it and reducing its activity. However, as compared to mechanically stirred system, the ultrasonic system showed ~30 % reduction in activation energy, which could be a consequence

of the mass transfer enhancement in the system. The optimum value of alcohol molar ratio of 11 could be justified as follows: For very low catalyst concentration (3 wt%), the amount of methoxy ions generated is low, resulting in smaller yields. Although stronger dispersion and emulsification between oil and methanol phases is achieved at high alcohol molar ratio, the mass transfer resistance for CH_3O^- ions increases. Higher mass transfer resistance can be explained as follows: CH_3O^- ions are generated at the surface of CaO catalyst. The CaO catalyst particles, being hydrophilic in nature, preferentially stay in the methanol phase. As the volume fraction of methanol in the total reaction mixture increases with molar ratio, these ions have to diffuse through larger volume so as to reach the interface and react with triglyceride. For low alcohol molar ratios, the volume fraction of oil in reaction mixture is high and some catalyst particles may also stay in oil phase. The oil can wet the catalyst surface, and hinder adsorption of methanol leading to formation of methoxy ions.

4. Choudhury et al. [75] have also reported a novel single step process for biodiesel synthesis using chlorosulphonic acid as catalyst. The previous process with H_2SO_4 catalyst [73] requires a two stage approach with esterification and transesterification. However, with chlorosulfonic acid as the catalyst, two steps process is combined in a single step process. The chemical mechanism of this synthesis is shown in Scheme 2.3. The acid catalyzed esterification of the free fatty acids in *Jatropha* oil releases water, which has serious inhibition effects due to solvation of the protons as well as CH_3OH_2^+ (methoxenium) ions. Solvation of the protons reduces their reactivity and accessibility leading to lowering of kinetics. The chlorosulphonic acid counteracts this inhibition by in situ removal of water formed during esterification. Water produced in the esterification process reacts with chlorosulfonic acid to produce H_2SO_4 . Dissociation of this H_2SO_4 can generate additional protons that catalyze esterification/transesterification reaction. However, generation of H_2SO_4 is accompanied by in situ removal of water molecules that solvate the H_3O^+ ion and reduce its activity. In this study as well, the statistical design of experiment was used to determine the optimum condition for the highest biodiesel yield. The optimum conditions are: catalyst concentration = 8.358 wt%, alcohol molar ratio = 18:1 and temperature = 60 °C.

The optimum temperature was close to boiling point of methanol, and also that the intensity of transient cavitation is minimal at this temperature, once again demonstrates that the beneficial effect of ultrasound and cavitation on reaction system was merely physical, that is emulsification of the phases. The activation energy for the single-step process was determined as 57.3 kJ/mol, which is more than three-fold lower than for H_2SO_4 catalyzed process (i.e. 169 kJ/mol). Choudhury et al. [75] also carried out chlorosulfonic acid catalyzed transesterification in conventional two-step process comprising of esterification and transesterification. Quite interestingly, the two-step process had 40 % less activation energy of 31 kJ/mol. This reduction has been attributed to complete removal of water from reaction system in the two-step process—as compared to single step process, in which some trace of water might be left in the system despite the in situ removal of chlorosulfonic acid, which reduces inhibition effect on the process.



Scheme 2.3 **a** Reaction of chlorosulfonic acid induced esterification process, **b** removal of water formed during esterification by chlorosulfonic acid, and **c** mechanism of chlorosulfonic acid induced transesterification process. Reprinted with permission from [75], Copyright © 2014, Wiley

The six studies on ultrasonic synthesis of biodiesel published reviewed in this section clearly reveal that the beneficial effect of ultrasound and cavitation on the transesterification reaction system is mainly physical as the reaction system is governed by intrinsic kinetics, through the alcohol to oil molar ratio, catalyst concentration and temperature.

2.4.3 Bioconversion of Crude Glycerol

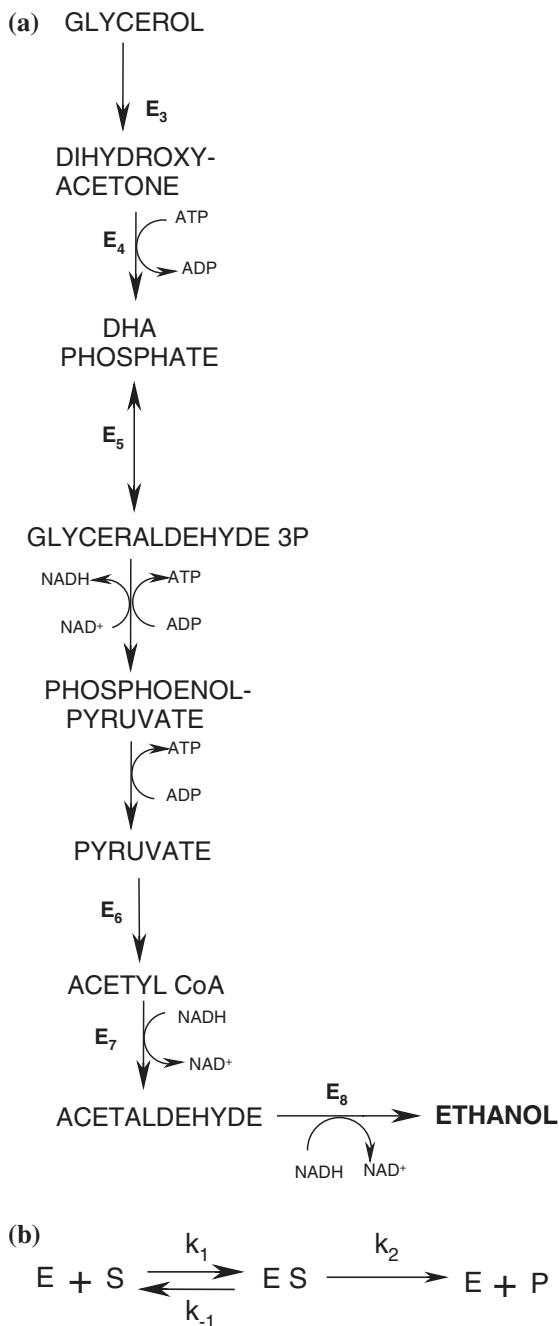
The transesterification reaction for biodiesel synthesis produces glycerol as the product. Transesterification of 1 mol of triglyceride with 3 mol of alcohol yields 3 mol of fatty acid alkyl ester (which is biodiesel) and 1 mol of glycerol. On a

weight basis, 1 kg of crude glycerol is produced per 9 kg of biodiesel. However, this glycerol is contaminated with alkali and alcohol, and is not useful for conventional applications such as cosmetics. Purification costs of this glycerol are prohibitively high. With biodiesel industry growing at an unprecedented rate all over the world, effective and efficient utilization of billions of gallons of crude glycerol is a daunting challenge before biodiesel industry. Glycerol, however, is an excellent carbon source for fermentation. Catalytic conversion of glycerol to other value-added products has also been extensively investigated. Forward integration of the biodiesel industry to convert crude glycerol to value-added products is a potential means of effective utilization of glycerol, as well as improvement of the economy of biodiesel industry with additional revenue fetched by these products. We have conducted investigations in the bioconversion of glycerol to three products, viz. 1,3-propanediol, butanol and ethanol, using immobilized cultures of *Clostridium pasteurianum*. Our approach has been to develop a complete process for this conversion, including optimization and intensification with ultrasound. Below is the summary of our investigations in ultrasonic enhanced bioconversion of glycerol. After initial optimization of culture growth medium and physical parameters for fermentation [76–78], Khanna et al. [79] have carried out mechanistic investigations in ultrasound enhanced glycerol bioconversion using free cells of *Clostridium pasteurianum*. The experimental results were analyzed *vis-à-vis* the simulation of cavitation bubble dynamics. Experiments were carried out in a specially designed test tube with provision of raising the static pressure to eliminate the transient cavitation in the system, which is harmful for microbial cells. The control experiments were carried out in an incubator shaker. The morphological changes in the microbial cells in control (mechanical shaking) and test (sonication) were assessed using flow cytometry. The influence of ultrasound on glycerol bioconversion was assessed using enzyme kinetics. The metabolic pathway of glycerol bioconversion to 1,3-PDO and ethanol is shown in Schemes 2.4a and 2.5a, respectively. The metabolic pathway for 1,3-PDO involves only one intermediate, while ethanol pathway involves multiple intermediates. The enzymes in the pathway for 1,3-PDO are inhibited by substrate (glycerol) as well as 3-hydroxypropionaldehyde (the intermediate), while no such effect is seen for the metabolic pathway for ethanol. Therefore, influence of ultrasound on ethanol production was assessed using Michaelis–Menten model, while 1,3-PDO production was evaluated using substrate inhibition or Haldane kinetics model. Before proceeding to the results and discussion of study of Khanna et al. [79], we give herewith a description of these models for general readers. The equation for Michaelis–Menten model is given below (Eq. 2.7) with scheme depicted in Scheme 2.4b.

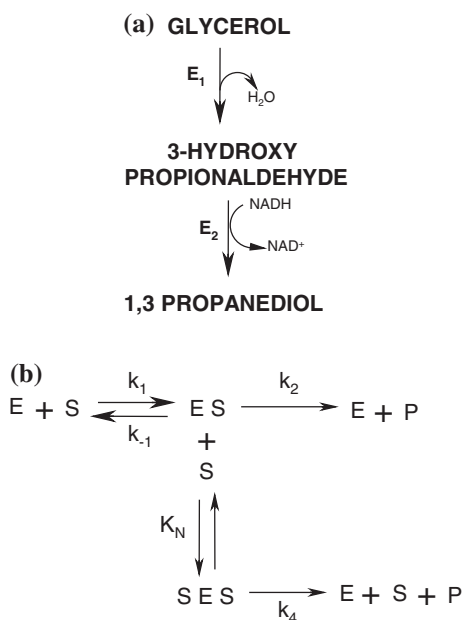
$$V = \frac{k_2 E_0 [S]}{K_m + [S]} = \frac{V_{\max} [S]}{K_m + [S]} \quad (2.7)$$

where k_1 , k_{-1} and k_2 are kinetic constants, K_m is the Michaelis constant and is defined as $(k_2 + k_{-1})/k_1$ and approximated as k_{-1}/k_1 under rapid equilibrium conditions, $k_{-1} \gg k_2$.

Scheme 2.4 a Metabolic pathway for glycerol bioconversion to ethanol (Enzymes: E3 = Glycerol dehydrogenase Type I; E4 = Dihydroxyacetone kinase; E5 = Triose phosphate isomerase; E6 = Pyruvate dehydrogenase complex; E7 = Acetaldehyde dehydrogenase; E8 = Alcohol dehydrogenase), **b** Michaelis–Menten reaction scheme. Reprinted with permission from [79], Copyright © 2012, Elsevier



Scheme 2.5 a Metabolic pathway for glycerol bioconversion to 1,3-PDO (Enzymes: E_1 = Glycerol dehydratase; E_2 = 1,3-PDO dehydrogenase); **b** Haldane reaction scheme for substrate inhibited conversion. Reprinted with permission from [79], Copyright © 2012, Elsevier



In Haldane substrate inhibition kinetics, the enzyme is assumed to have two binding sites for its substrate S —one catalytic site for binding that can produce a product, P ; and the second non-catalytic site that can produce a product at reduced rate. The complex formed by binding of substrate to catalytic site is denoted by $E \cdot S$, while $S \cdot E \cdot S$ denotes the complex with two substrate molecules bound to both catalytic and non-catalytic site. The reaction scheme for Haldane kinetics is depicted in Scheme 2.5b. Haldane considered a simple case in which binding of substrate to catalytic site precedes the binding to non-catalytic site, and further that K_4 (the kinetic constant of product formation through $S \cdot E \cdot S$ complex) to be zero. With assumption of rapid equilibrium for $E \cdot S$ complex formation, Haldane [80] derived following kinetic expression (Eq. 2.8) for substrate inhibited reaction scheme:

$$V = \frac{k_2 E_0 [S]}{K_m + [S] + \frac{[S]^2}{K_I}} = \frac{V_{\max} [S]}{K_m + [S] + \frac{[S]^2}{K_I}} \quad (2.8)$$

where, K_I is the dissociation equilibrium ($1/K_N$) for the reaction $S \cdot E \cdot S \leftrightarrow S + E \cdot S$. The above expressions indicate that reaction velocity goes to zero as the substrate concentration $[S]$ becomes large, due to significant amount of enzyme being engaged in non-productive complex. The constants in the kinetic expressions have physical significance. Low values of K_m indicate greater affinity of enzyme towards substrate, while high values of K_I indicate greater tendency of enzyme towards substrate binding to non-catalytic site that leads to inhibition. High value of $V_{\max}$ indicates greater tendency of $E \cdot S$ complex to split into the

products. Comparative evaluation of these constants for the experiments with mechanical shaking and ultrasound gives a mechanistic account of the influence of ultrasound on bioconversion process. The kinetic data of glycerol conversion into 1,3-PDO and ethanol with different substrate concentrations was fitted to the enzyme kinetics models to get physical insight into the influence of ultrasound.

The major results of this study are summarized in Table 2.3, which shows the complete material balance for glycerol conversion for 3 different initial glycerol concentrations, viz. 5, 10 and 25 g/L, along with the yield and selectivity of products and the constants in enzyme kinetics models. Assessment of the morphology of microbial cells with flow cytometry and microscopic analysis (Figs. 2.7 and 2.8) revealed no adverse effect of sonication or elevated static pressure on cells. Moreover, the cell population in the medium as determined by the optical density was also found to stay constant during the test period. The typical trends of glycerol bioconversion are as follows.

1. Glycerol uptake by the microbial cells remained unaltered with sonication, while the glycerol utilization (product formation) showed significant rise with sonication.
2. Highest percentage of glycerol utilization was seen for an initial concentration of 10 g/L. Due to substrate inhibition, the amount of unutilized glycerol was the highest for an initial concentration of 25 g/L.
3. Production of both 1,3-PDO and ethanol increases with ultrasound. Percentage enhancement of yield for ethanol shows a monotonous increase with initial glycerol concentration, while enhancement of yield of 1,3-PDO shows a maximum for an initial concentration of 10 g/L. The yield was the lowest for 25 g/L glycerol, as large quantity of glycerol remained unutilized.

These experimental trends were analyzed *vis-à-vis* the simulation of bubble dynamics. In absence of transient cavitation, the rapid oscillatory motion of microbial cells due to micro-streaming may cause collisions among cells or with the walls of the reactor vessel. This phenomenon could help enhance the metabolism and utilization rate of glycerol. Moreover, ultrasound can also enhance desorption of the gaseous products of metabolism from medium, thus causing enhancement in the kinetics of the metabolic reactions.

Comparative evaluation of enzyme kinetic parameters for ethanol and 1,3-PDO in test and control experiments, and their manifestation on the yield and selectivity gives a physical insight into the influence of ultrasound on the bioconversion. Due to faster diffusivity of glycerol into microbial cells, the overall enzymatic reaction system or metabolic pathway is always expected to be substrate saturated, with enzyme being limiting reactant.

1. The Michaelis–Menten constant for ethanol formation reduces with ultrasound, which indicates higher substrates affinity and faster formation of $E \cdot S$ complex. But the value of $V_{\max}$ indicating splitting of the $E \cdot S$ complex into products also getting reduced. Nonetheless, greater formation of the $E \cdot S$ complex still drives enhancement in ethanol formation.

Table 2.3 Material balance for glycerol bio-conversion

Final concentrations (mM)	Initial glycerol concentration					
	5 g/L (54.4 mM)		10 g/L (108.7 mM)		25 g/L (271.7 mM)	
	Ultrasound	Without ultrasound	Ultrasound	Without ultrasound	Ultrasound	Without ultrasound
Ethanol	2.12 ± 0.13	1.74 ± 0.07	11.33 ± 0.22	7.29 ± 0.19	10.58 ± 0.32	5.78 ± 0.05
1,3 Propanediol	2.98 ± 0.01	2.33 ± 0.18	4.76 ± 0.15	3.19 ± 0.10	5.47 ± 0.26	4.18 ± 0.10
Glycerol uptake ^a	48.6	48.4	91	91.5	262	244
Glycerol consumption ^a (Stoichiometric)	5.1	4.07	16.09	10.48	16.05	9.96
Residual glycerol ^a in cells	43.5	44.33	74.91	81.02	245.95	234.04
Percentage enhancement in glycerol consumption with ultrasound ^a	25.3	N.A.	53.5	N.A.	61.1	N.A.
Percentage glycerol utilized ^a	10.5	8.4	17.7	11.5	6.1	4.1
Percentage glycerol remained unutilized ^a	89.5	91.6	82.3	88.5	93.9	95.9

N.A. not applicable
^a Calculated using mean values of ethanol and 1,3-PDO production
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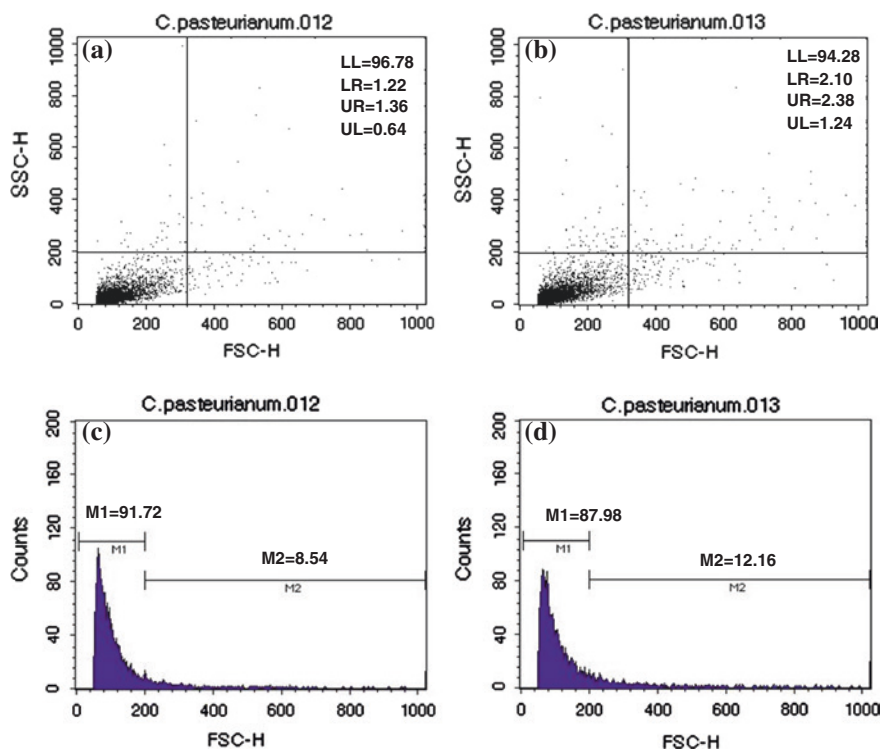


Fig. 2.7 Flow cytometric analysis for estimation of morphological changes **a** and **b** acquisition dot plots (forward-scattered light vs. side-scattered light) of *C. pasteurianum* cells in control and test samples respectively. **c** and **d** Histogram plots (counts vs. FSC) of *C. pasteurianum* in control and test samples cells respectively. As there is no significant change in FSC after sonication as shown by both plots, therefore morphology of cells remains same. Reprinted with permission from [79], Copyright © 2012, Elsevier

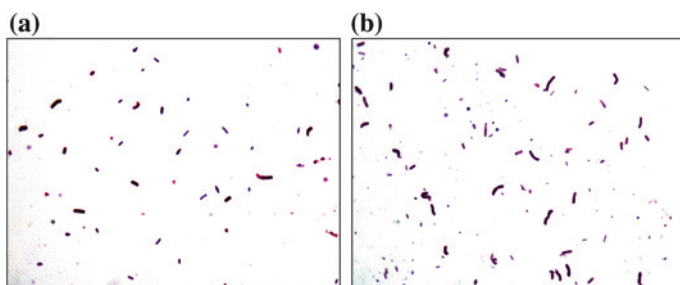


Fig. 2.8 Morphology of cells of *Clostridium pasteurianum* **a** before sonication, and **b** after sonication. As there is no significant change in FSC after sonication as shown by both plots, therefore morphology of cells remains same

- For 1,3-PDO formation, the Michaelis–Menten constant increases with ultrasound indicating reduced substrate affinity and reduced formation of $E \cdot S$ complex. Reduction in the inhibition constant K_i indicates greater tendency of binding of $E \cdot S$ complex to non-catalytic site and formation of non-productive $S \cdot E \cdot S$ complex. On the contrary, the reaction velocity increases with ultrasound, signifying higher rate of splitting of the $E \cdot S$ complex into products. Despite these counter-productive variations in kinetic parameters, the overall rate of 1,3-PDO production increases—which is attributed to saturation of the cells with substrate due to its faster intrinsic diffusivity into the cells. However, due to greater substrate inhibition seen with ultrasound, the extent of percentage enhancement is much less than that seen for ethanol—where enzymes are not inhibited by the substrate.

All of these results pointed that convection generated by ultrasound and cavitation enhances the rates of enzymatic reactions in the pathway of glycerol conversion. However, the biochemistry of metabolic pathway of glycerol conversion is not affected by ultrasound, as the exactly same profiles in terms of absolute rate of production and yield are seen with ultrasound and mechanical shaking. Thus, the role of ultrasound and cavitation is found to be of physical nature.

Khanna et al. [81] extended the theme of ultrasonic enhancement of glycerol bioconversion with immobilized culture of *Clostridium pasteurianum* on silica support. A similar approach of assessing effect of ultrasound with enzyme kinetics models was adopted. The kinetic constants determined from Michaelis–Menten and Haldane kinetics model are listed in Table 2.4. The major conclusions of this study, which showed distinct differences from the results observed for free cells, are summarized below:

- The dominant product of glycerol bioconversion using immobilized cells was 1,3-PDO. This was a consequence of favorable change in kinetic parameters for immobilized cells under ultrasound as seen from Table 2.4. The inhibition constant K_i increased (indicating reduction in inhibition), while the Michaelis–Menten constant K_m reduced (indicating increase in substrate affinity) under sonication, which essentially promoted the glycerol conversion through metabolic pathway indicated in Scheme 2.5a, b. The total product concentration for immobilized cells was higher than free cells, which is attributed to greater tolerance of immobilized cells towards substrate inhibition. In this study, the individual enhancement effect of ultrasound for immobilized cells was lower, as the technique of immobilization itself counteracted inhibition to large extent.

Table 2.4 Enzyme kinetics parameters for Ethanol dehydrogenase and 1,3-PDO dehydro-genase

Kinetic parameters	Ethanol dehydrogenase		1,3-PDO dehydrogenase	
	Test	Control	Test	Control
$V_{\max}$ (mM/min)	0.016	0.016	0.023	1.699
K_m (mM)	1.1	1.1	16.56	3,691.90
K_i (mM ⁻¹)	N.A	N.A	1,036.14	1.61

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2. The immobilization of cells coupled with sonication caused a major shift of selectivity through predominant pathway of glycerol conversion. Although the metabolic pathway for ethanol was multi-step, involving several enzymes and intermediates, there was no limitation of inhibition (either substrate or product). On the other hand, although the metabolic pathway for 1,3-PDO was single step, it suffers from both substrate and product inhibition of the enzyme, 1,3-PDO dehydrogenase. Immobilization as well as sonication reduced the inhibition significantly, which essentially resulted in shift of preferable pathway to 1,3-PDO.
3. The enhancement effect of ultrasound for ethanol was rather negligible for immobilized cells as the same value of reaction velocity and Michaelis–Menten constant were observed with mechanical shaking and sonication.
4. Maximum percentage enhancement of glycerol bioconversion for immobilized cells was seen for the highest glycerol concentration of 25 g/L—as against moderate concentration of 10 g/L seen for free cells.

The investigations of Khanna et al. [79, 81] have corroborated the physical influence of ultrasound and cavitation on glycerol bioconversion system. Coupling of sonication with other process alternatives like immobilization of cultures can have great beneficial effects on glycerol bioconversion.

2.4.4 Ultrasonic Desulfurization

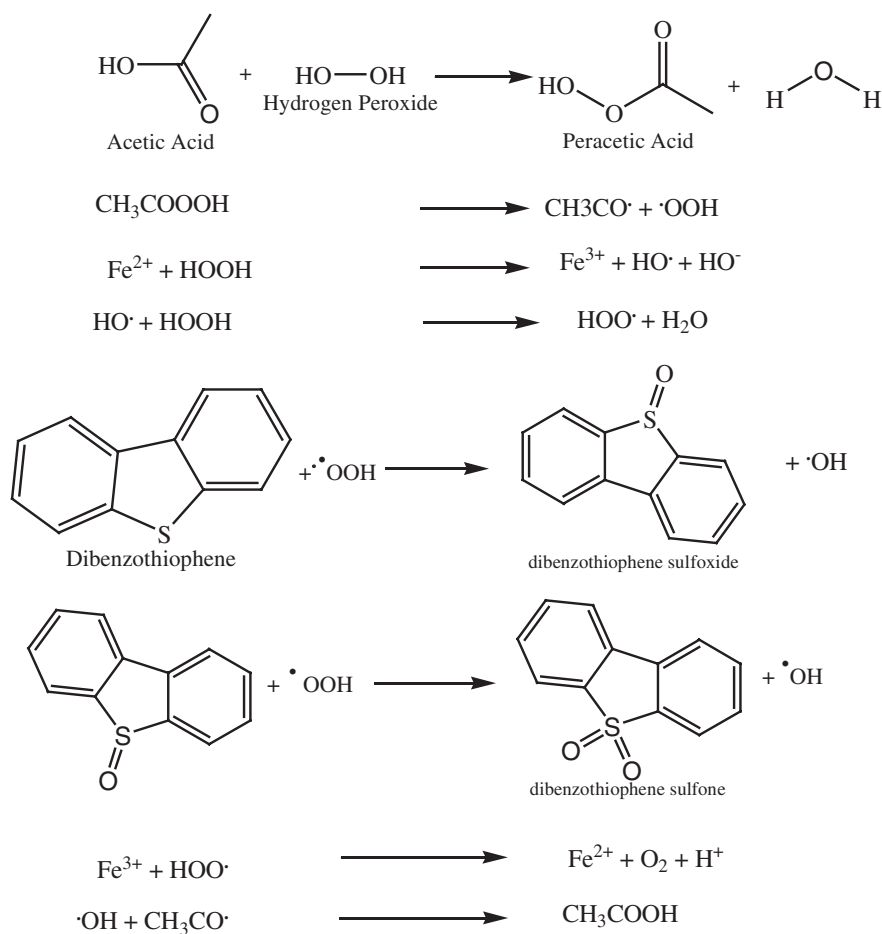
Oxidative desulfurization is the new technology for the removal of sulfur compounds from liquid transportation fuels. The sulfur content of biofuels is relatively much less than petroleum fuels. Yet, in some cases where the feedstock for biofuels itself contains sulfur impurities, and hence, desulfurization becomes a necessary step in the downstream processing. In oxidative desulfurization, the sulfur containing compounds are initially oxidized to sulfones and the sulfones are extracted using suitable solvent like dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), acetonitrile or methanol. Oxidative desulfurization has several distinct merits over conventional hydro-desulfurization in that it does not require expensive hydrogen. The treatment conditions of ambient temperature and pressure and effective desulfurization of substituted sulfur compounds can be achieved which is difficult with conventional hydro-desulfurization due to low reactivity of these compounds. The reaction system of oxidative desulfurization is liquid–liquid heterogeneous type in which the oxidant is in the form of peroxyorganic acids, hydroperoxides or peroxy salts and is in the aqueous phase, while the sulfur compounds are in the form of sulfides, thiols, thiophenes, benzothiophene, dibenzothiophene and their substituted derivatives and are in the organic phase. Several studies have been published in the recent past, which have reported the beneficial influence of ultrasound on the enhancement of oxidative desulfurization. We have conducted the same studies recently that have shed light on the exact physical mechanism of ultrasound enhanced oxidative desulfurization.

Bolla et al. [82] investigated oxidative desulfurization of three sulfur compounds, viz. thiophene, benzothiophene and 3-methyl thiophene with peroxy acetic acid and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as oxidants and n-hexane as model liquid fuel. The experiments were conducted in an ultrasound bath with frequency of 35 kHz and power of 35 W with pressure amplitude of the ultrasound wave being 150 kPa. The major experimental variable was system pressure. Experiments were conducted at two static pressures, viz. atmospheric (101.3 kPa) and elevated (250 kPa). Simulations of cavitation bubble dynamics in n-hexane were carried out to estimate the peak temperature and pressure conditions reached during transient collapse and the chemical species generated in the bubble during collapse. The major conclusions of this study were as follows:

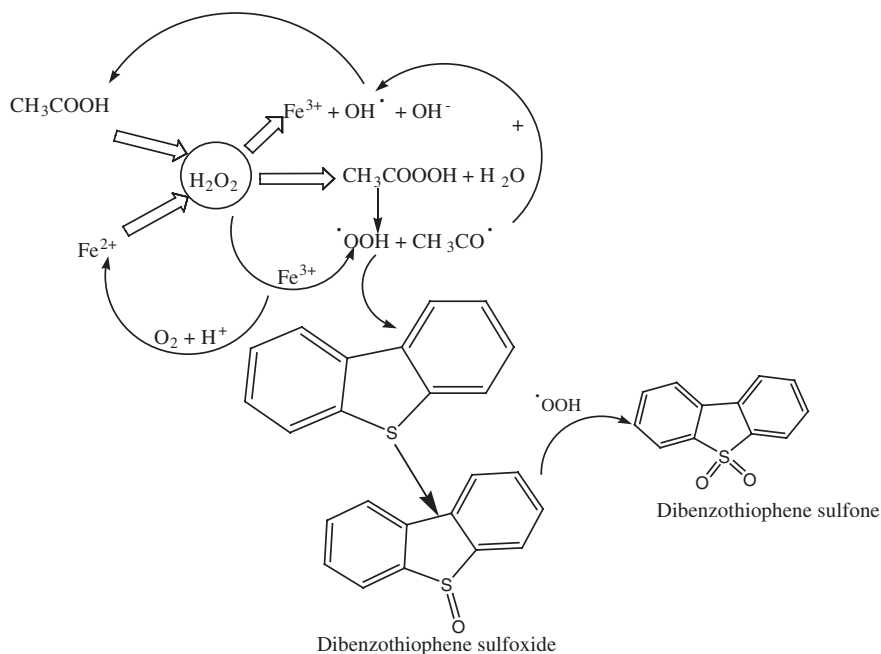
1. Time profile of oxidation for all sulfur compounds (and for all 3 levels of initial concentrations) followed first order kinetics;
2. Transient collapse of cavitation bubble in n-hexane was not intense enough to generate any radical species;
3. Higher rates of oxidation were obtained with peracetic acid coupled with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.
4. Most interestingly, higher kinetics as well as extent of oxidation was achieved for all sulfur compounds in experiments at elevated static pressure of 250 kPa.

An explanation for these results can be given along following lines: Large evaporation of n-hexane vapor in the bubble reduces the intensity of the transient collapse of the bubble. Due to lower temperature and pressure peaks reached during transient collapse, the main species generated from thermal dissociation of n-hexane were H_2 , CO, CH_4 . Higher oxidation rates in presence of peracetic acid and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ mixture was attributed to additional generation of the oxidant species by reaction of $\cdot\text{OH}$ radicals generated from Fenton's reactions with dissolved in the system ($\cdot\text{OH} + \text{O}_2 \rightarrow \text{HO}_2\cdot + \text{O}\cdot$). This effect essentially is the conservation of radical species in the system, which leads to their effective utilization in the reaction. Higher kinetic and yield of oxidation at elevated static pressure could be explained on the basis of the simulation of cavitation bubble dynamics. The predominant species generated from thermal dissociation of n-hexane in the cavitation bubble at transient collapse are H_2 and CO. These species can competitively consume $\text{O}\cdot$ species generated by the oxidant. Thus, utilization of $\text{O}\cdot$ species towards oxidation of sulfur compound is limited, which results in the reduction in the extent of oxidation. With application of elevated static pressure, the transient cavitation in the system is eliminated, and hence, the formation of H_2 and CO. The oxidant species are thus effectively utilized for desulfurization. As far as the physical effect of intense micro-mixing and emulsification that facilitates interphase mass transfer is concerned, the contribution by micro-streaming due to ultrasound is more than microturbulence due to cavitation. The ultrasound wave phenomena is unaffected by the static pressure, and hence, the interfacial area between organic and aqueous phase at the two pressure levels stays practically unaltered. The results of Bolla et al. [82] clearly revealed the physical mechanism of ultrasonic oxidative desulfurization.

In a subsequent publication, Bhasarkar et al. [83] studied oxidative desulfurization with sono-Fenton–peracetic acid system as oxidant. The model fuel used in this work was toluene, which has significantly different physical properties than n-hexane used in the previous study. The overall reaction scheme for the oxidative desulfurization and the links between different chemical species are shown in Schemes 2.6 and 2.7, respectively. Simulations of cavitation bubble dynamics were carried out for both peracetic acid and toluene as the liquid medium. In addition to static pressure of the system, additional optimization parameters were: (1) acetic acid to H_2O_2 molar ratio, (2) volume ratio of organic and aqueous phases, (3) loading of iron catalyst and (4) excess H_2O_2 . This study, which spanned more process variables and alternatives, revealed further features of ultrasonic oxidative desulfurization. Simulation results revealed that transient collapse of bubble was

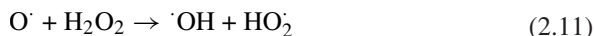
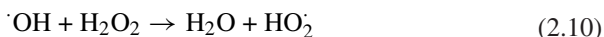
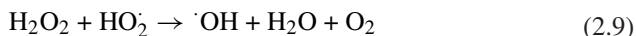


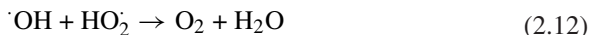
Scheme 2.6 Reaction scheme for oxidative desulfurization. Reprinted with permission from [83], Copyright © 2013, American Chemical Society



Scheme 2.7 Links or interactions between different chemical species in peracetic acid—Fenton process for oxidative desulfurization. Reprinted with permission from [83], Copyright © 2013, American Chemical Society

quite intense and peak temperature and pressure conditions reached in the bubble for both peracetic acid and toluene as the medium were sufficiently high to cause generation of radical oxidant species like $O^\cdot$ and $HO_2^\cdot$. This result was attributed to low vapor pressure of toluene and peracetic acid. At elevated pressure, the intensity of transient collapse reduced sharply, but due to very low evaporation of toluene/peracetic acid in the bubble, the species were mainly CO_2 and H_2O , which would not hinder the oxidative desulfurization. The chemistry of oxidative desulfurization in this case was complicated due to different sources of radicals (viz. $O^\cdot$, $HO_2^\cdot$ and $^\cdot OH$) in the process, i.e. cavitation bubbles, peracetic acid and Fenton reaction. The most effective radical species for oxidative desulfurization is $HO_2^\cdot$. Different possible reactions between the radicals can result in scavenging of $HO_2^\cdot$ radicals before their utilization for oxidative desulfurization as follows (Eqs. 2.9–2.13):

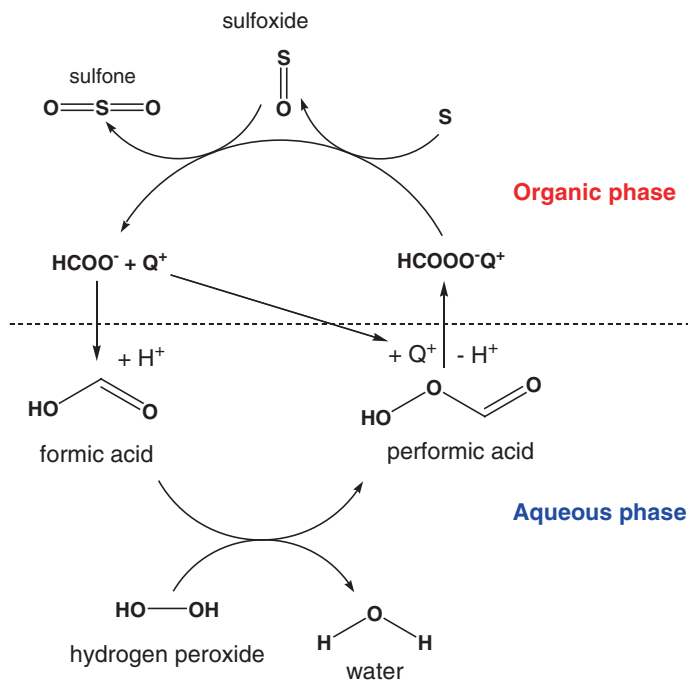




The major results of this study and their explanations on the basis of bubble dynamics simulations are as follows:

Addition of Fe^{2+} to reaction system showed greater enhancement for mechanically stirred system than sonicated system. This clearly indicated that mass transfer characteristics of the system have more influence on the reaction system than the chemical kinetics. $\cdot\text{OH}$ radical production by Fenton process causes regeneration of acetic acid (by combining with $\text{CH}_3\text{CO}\cdot$ radical), which further enhances $\text{HO}_2\cdot$ radical production. However, less enhancement of oxidation with Fe^{2+} for ultrasonic system clearly indicates that effective interphase transfer of $\text{HO}_2\cdot$ radicals is more important than mere generation of these radicals. Reduction of oxidation with excess H_2O_2 was also an unexpected result of this study. This is attributed to scavenging of the $\text{HO}_2\cdot$ radicals by H_2O_2 through reactions mentioned earlier. The rise in oxidation yield at elevated static pressure is attributed to elimination of production of $\cdot\text{OH}$ and $\text{O}\cdot$ radical species, which scavenge the $\text{HO}_2\cdot$ species.

Bhasarkar et al. [84] have also studied the influence of phase transfer agent on ultrasound enhanced oxidative desulfurization simultaneously. The model system used was toluene as the model fuel, dibenzothiophene as the model sulfur compound, tetra octyl ammonium bromide (TOAB) as the phase transfer agent, and two oxidation systems, viz. peracetic acid and performic acid. The results of different operational variables on ultrasonic oxidative desulfurization system were compared against mechanically agitated system. The beneficial action of PTA on the oxidative desulfurization system is shown in Scheme 2.8. The influence of PTA on the enhancement of oxidation was more pronounced for mechanically agitated system. This result has been attributed to faster mass transfer characteristics of sonicated system due to fine emulsification, due to which the additional effect of enhancement of interphase mass transfer by PTA is limited. Comparing between performic acid and peracetic acid, the extent of oxidation was higher for performic acid, and this result is attributed to relatively faster diffusion of performic acid-PTA complex due to smaller size. Addition of excess H_2O_2 in this case caused reduction in the extent of oxidation. This effect was not only attributed to scavenging of radicals, but competitive formation of H_2O_2 -PTA complex in addition to peracetic acid-PTA complex. Finally, the beneficial effect of elevated static pressure is reduced in the presence of PTA, as noted earlier. Elevation of static pressure eliminates transient cavitation responsible for the formation of molecular and radical species in the organic phase that competitively consume the oxidant. However, in the present situation, the PTA assists efficient transfer of oxidant species across interface, and thus, helps mitigate the adverse effect of reducing/scavenging species.



Scheme 2.8 The cyclic mechanism of phase transfer agent (PTA) during oxidative desulfurization with perorganic acid (e.g. performic acid)

2.4.5 Biomass Pretreatment

Lignocellulosic biomass derived biofuels have been extensively investigated in the past few decades. Synthesis of alcoholic biofuels like ethanol, butanol requires pretreatment and hydrolysis of biomass to release fermentable sugar. The biomass is subjected to several physical and chemical treatments for pretreatment and sugar release. The physical treatments are grinding, milling, water bath treatment, steam explosion or autoclaving. These techniques are coupled with acid or alkali for the removal of hemicelluloses and lignin components, respectively. The lignocellulosic biomass comprises of lignin, hemicelluloses and cellulose. The dense layers of lignin prevent accessibility of cellulose during enzymatic hydrolysis to release hexose sugars. The hydrolysis of hemicellulose is carried out under acidic pretreatment, and this hydrolysis releases pentose sugars. The pretreated biomass after removal of lignin and hemicelluloses is hydrolyzed using enzymes. All three steps of pretreatment, viz. acid hydrolysis, alkaline delignification and enzymatic hydrolysis have been intensified using ultrasound. We have carried out mechanistic investigation of these systems that are summarized next.

Suresh et al. [85] have investigated the mechanics of hybrid techniques for treatment of rice straw prior to fermentation to alcohol liquid fuels. Two chemical techniques viz. dilute acid and dilute alkali treatment and two physical techniques viz. hot water bath and autoclaving were coupled with sonication. The efficacy of each sono-hybrid was assessed on the basis of total sugar and reducing sugar release. The total sugar released during acid and alkali hydrolysis consists of sugars in any form, viz. monomer sugars (i.e. pentose sugars like xylose and arabinose, and hexose sugars like glucose and mannose), oligomers (cellobiose) and dehydrated forms that form at low pH from xylose and glucose like furfural and hydroxy methyl furfural. The reducing sugar fractions of total sugar essentially are the monomeric sugars. During experiments, elevated static pressure was applied to discriminate between physical and chemical effects of ultrasound and cavitation. The mathematic model used in this study included not only the micro-streaming, microturbulence and shock wave effects, but also the acoustic streaming near the boundaries. Nyborg [57] presented the pioneering analysis of steady circulations induced by high amplitude sound fields near surfaces of obstacles and vibrating elements and bounding walls. Nyborg et al. [57] proposed that gas comes out of solution under influence of ultrasound at solid-liquid surfaces that leads to the formation of gas nuclei on the surface. The oscillatory velocities of liquid induced by volume oscillations of these gas bodies can be an effective source of highly localized streaming. The near boundary limiting velocity of micro-streaming flow over plain surfaces was determined as (Eq. 2.14):

$$U_L = (1/4\pi^2\omega)(Q^2/r^5) \quad (2.14)$$

where Q is the volumetric flow rate and r is the distance from boundary. Applying this analysis for the present situation of hydrolysis of biomass, a pulsating hemispherical bubble was taken as basis and the micro-streaming velocity was determined as follows (Eq. 2.15):

$$U_{ms} = (U^2/\omega R) \quad (2.15)$$

where U is the velocity amplitude of oscillations of fluid elements, ω is the angular frequency of acoustic wave and R is the radius of the bubble. For acoustic pressure amplitude of 150 kPa, the velocity of fluid elements is 0.1 m/s. For an ultrasound frequency of 35 kHz as used by Suresh et al. [85] and 5 μ m size bubble trapped in the biomass matrix, the localized micro-streaming velocity is 0.09 m/s. The main results of the study of Suresh et al. [85] are summarized as below:

1. The physical technique of autoclaving alone did not give significant sugar release. However, coupled with sonication after autoclaving, the sugar release increased markedly.
2. Sonication after autoclaving in acidic environment results in doubling of the sugar release. However, raising the static pressure of the system is revealed to reduce the sugar release.

3. Highest sugar release (~54 %w/w rice straw) was obtained for autoclaving, stirring followed by sonication in an acidic environment. As per the composition of rice straw, this was the highest possible sugar yield from rice straw with hydrolysis of all cellulose and hemicelluloses components of biomass.

Before interpretations of the results, the chemical mechanism of different reactions occurring during biomass pretreatment needs to be considered. Autoclaving causes hydrolysis of hemicelluloses in biomass that results in the formation of organic acids like acetic acid and other acids that can form the acetyl and other functional groups released from biomass. Water itself promotes hydrolysis at elevated temperatures due to change in ion product that assists in reaction of hemicelluloses. Autoclaving also causes rapid thermal expansion of biomass that helps opening up of the biomass structure with an increase in pore volume. Hot water bath treatment enhances cellulose digestibility and sugar extraction. Dilute acid treatment results in the solubilization of hemicelluloses leaving lignin and cellulose intact, which helps in increasing the accessibility of cellulose for the further enzyme treatment. Under optimized conditions, oligomeric hemicelluloses saccharides can be completely hydrolyzed to monosaccharides giving high xylose yield.

Alkaline pretreatment is mainly aimed at delignification but it also causes partial hydrolysis of hemicelluloses. The main chemical mechanism of alkaline treatment is saponification of intermolecular ester bonds cross linking xylan hemicelluloses, other celluloses and lignin. Acetyl and uronic acid substitutions on hemicelluloses are removed during alkaline treatment. In addition to these, other effects of alkaline treatment are swelling of biomass resulting in reduction in the degree of polymerization as well as crystallinity, increase in the surface area, disruption of lignin structure and the structural linkages between lignin and carbohydrates.

Overall, the biomass hydrolysis system is mass transfer controlled. Jacobson and Wyman [86] have presented a hypothesis of mass transfer problem in biomass pretreatment. Long chain cellulose are less soluble in water than short chain oligomers formed as intermediates during hydrolysis, but solubility of both reduces with temperature. If liquid continuously flows through the reaction system, the oligomers are removed continuously from the biomass matrix, which facilitates dissolution of more oligomers. This process increases the recovery of sugar monomers and oligomers, before they can degrade at the reaction conditions. If this is not done, re-precipitation of oligomers back onto surface of biomass may occur, due to less solubility at reduced temperature. Reactive lignin and sugar degradation products can promote reattachment of cellulose, hemicelluloses, their oligomers and lignin in the solution back to solid biomass, and these may also form complexes with monomeric sugars. Strong micro-convection generated ultrasound and cavitation cause effective circulation of water through biomass matrix with regular removal of monomeric sugars and refreshment of medium, which facilitates effective removal of sugar monomers. The radicals generated by transient bubbles can also assist higher sugar release due to cleavage of lignin carbohydrate

components. With this preamble of pretreatment mechanics, the main findings of Suresh et al. [85] were as follows:

1. Increase in autoclaving period of biomass did not enhance sugar yield. The extent of hydrolysis increases with time of autoclaving, but due to low convection, sugar molecules are not transported out of biomass matrix. Therefore, sugar concentration in the bulk medium does not change with increasing autoclaving periods. Sonication of the solution after autoclaving helps effective transport of sugar molecules out of biomass matrix.
2. Stirring of biomass solution for 24 h after autoclaving of 30 min does not increase the sugar yield. This result indicates two things: first, most of the hydrolysis of cellulose and hemicelluloses is completed during autoclaving itself, due to high temperature and pressure; and secondly, mechanical stirring of solution does not produce strong currents to penetrate biomass matrix causing sugar transport as happens in case of sonication.
3. Only slight reduction in the sugar yield at elevated pressure indicates negligible contribution of both physical and chemical effects of cavitation bubbles to the overall process of pretreatment and sugar release. The contribution by micro-streaming due to ultrasound and acoustic streaming had greater contribution to enhancement of the transport of sugar molecules. Neither the microturbulence nor the shock waves were intense enough to cause opening up of the biomass matrix and create liquid flow through the matrix that would assist sugar release. The opening of biomass structure is found to occur only with autoclaving (a thermal effect) and ultrasonic micro-streaming enhances the transport of sugar molecules.

In a subsequent study, Singh et al. [87] studied the delignification of waste biomass *Parthenium hysterophorus* with ultrasound. Optimization of the delignification of pretreated biomass (after dilute acid hydrolysis + autoclaving) was carried out with NaOH as delignifying agent. The optimization parameters were temperature, NaOH concentration and biomass concentration. Assessment of delignification (based on the determination of cellulose, hemicelluloses and lignin content of original and treated biomass) was done according to standard TAPPI protocols [88]. Characterization of delignified biomass was carried out using FTIR, XRD and FESEM analysis. The optimization values of parameters for delignification were: temperature = 303 K, NaOH concentration = 1.5 %w/w and biomass concentration = 2 %w/w. The chemical mechanism of delignification is as follows: Lignin is derived from three monomer units, viz. trans-coniferyl, trans-sinapyl and trans-*p*-coumaryl alcohol. These units are linked randomly mostly via ester linkages at α - and β -positions to construct the lignin macromolecules. The reactive sites in lignin are mainly the ester linkages and functional groups, since C–C are resistant to chemical attack. The areas of lignin susceptible to chemical attack are hydrolysable ester linkages, phenolic and aliphatic hydroxyl groups, methoxy groups, the unsaturated groups and uncondensed units. The major mechanism through which lignin degrades in alkaline environment is the cleavage of α - and β -aryl ether linkages. Ultrasound can cause depolymerization and separation of

lignin, in addition to degradation of lignin components. Ultrasonic depolymerization of lignin occurs through hemolytic cleavages of phenyl ether β -O-4 and α -O-4 bonds, while ultrasonic separation of lignin occurs through cleavage of lignin-hemicellulose linkages. The hydroxyl radical produced from transient cavitation bubbles can also contribute to degradation of lignin. The attack of $\cdot\text{OH}$ radical occurs on the aromatic ring leading to the formation of hydroxylated, demethoxylated and side chain eliminated products. A relatively small extent of attack can also occur on the side chain leading to the formation of dimers and oxidation of aromatic aldehydes to carboxylic acids. Increase in number of non-conjugated carboxyl also indicates hydroxyl radical induced degradation. Lignin condensation and re-polymerization can also occur under ultrasonic treatment.

The major findings of Singh et al. [87] are as follows:

1. The kinetics of delignification is enhanced more than two fold with ultrasound.
2. The extent of delignification with ultrasound was practically same in the range of 30–80 °C. At higher biomass concentration, the extent of delignification reduced, while leveling-off of delignification was seen with respect to NaOH concentration above 2 %w/w. On the basis of bubble dynamics simulations, these results were explained as follows: Although the intensity of transient cavitation reduces drastically with temperature, the intrinsic reactivity of OH^- increases, which compensates the effect, and thus delignification stays practically same in the temperature range of 30–80 °C. At large biomass concentration, scattering of the ultrasound wave occurs due to which the extent of convection generated in the system reduces. Strong convection generated by ultrasound and cavitation eliminates mass transfer in the system making biomass accessible to $\cdot\text{OH}^-$ ions. Thus, after a certain concentration of NaOH, leveling off of delignification is observed.

XRD analysis revealed reduction in the crystallinity index of biomass after delignification, which is attributed to depolymerization of cellulose with ultrasound with scission of β -1-4 glycosidic bonds that gives rise to short chains of glucose monomer units (Fig. 2.9). FTIR spectra of delignified biomass (Fig. 2.10) revealed reduction in the intensities of all bonds corresponding to lignin removal, rupture of cellulose bonds and carbohydrate-lignin linkages. Moreover, the bond intensities corresponding to aromatic ring stretching and cellulose band also reduced. Changes in the XRD and FTIR spectra of biomass after delignification are essentially manifestations of the physical and chemical effects of cavitation. Reduction in aromatic ring stretching and aromatic ring vibration bonds along with reduction in bonds corresponding to side chain removal are attributed to reactions induced by $\cdot\text{OH}$ radicals from transient cavitation. Transient cavitation also generates high pressure amplitude shock waves. The biomass particles get drifted randomly in these waves at high velocities leading to collision between them. The energy released in such collisions is sufficient to cause hemolytic cleavage of phenyl esters β -1-4 and α -1-4 bonds leading to depolymerization of lignin. Comparative analysis of FE-SEM pictures of delignified biomass with mechanical agitation and ultrasonication (Fig. 2.11) revealed more surface roughness of ultrasound treated

Fig. 2.9 X-ray diffractograms of *P. hysterophorus* biomass after different treatments. The crystallinity index of biomasses was determined as: original biomass = 57.36 %; delignified biomass with mechanical agitation = 46.9 %, delignified biomass with ultrasound = 45.9 %. Reprinted with permission from [87], Copyright © 2014, American Chemical Society

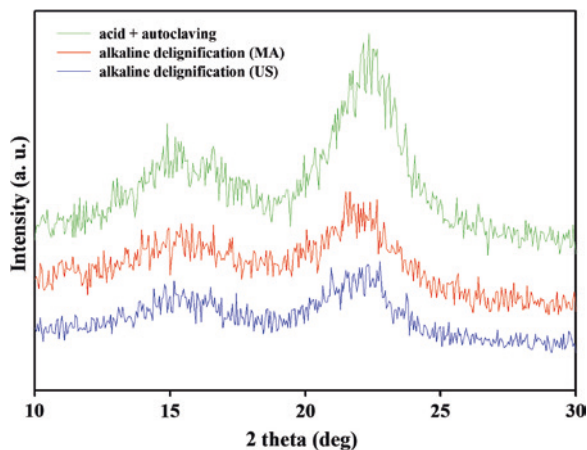
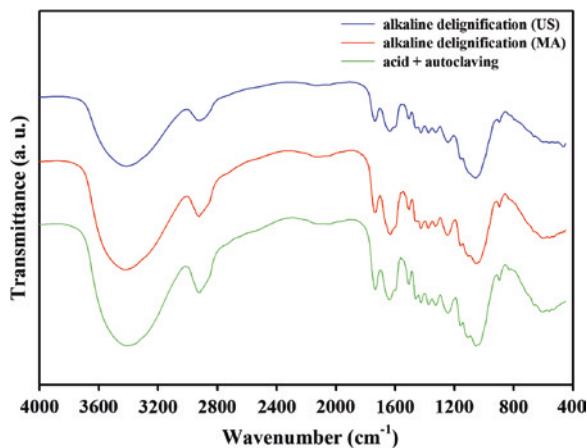


Fig. 2.10 FTIR spectra of *P. hysterophorus* biomass after different treatments (viz. alkaline delignification with and without ultrasound and acid + autoclaving). Reprinted with permission from [87], Copyright © 2014, American Chemical Society



biomass due to erosion or attrition. Thus, the study of Singh et al. [87] portrays a vivid picture of mechanistic facets of ultrasonic delignification.

Bharadwaja [89] have assessed the effect of ultrasound on enzymatic hydrolysis of delignified biomass. Two commercial enzymes, viz. cellulase and cellobiase, were employed for hydrolysis. Initially, statistical optimization of the enzymatic hydrolysis with mechanical shaking was carried out using Central Composite Design (CCD) coupled with Response Surface Method (RSM) analysis. The optimization parameters were the concentrations of the two enzymes and the biomass concentration. The temperature of the reaction mixture was 50 °C. Later, mechanical shaking was replaced with ultrasound. However, the temperature of reaction mixture was reduced to 30 °C for ultrasonic treatment, as the physical

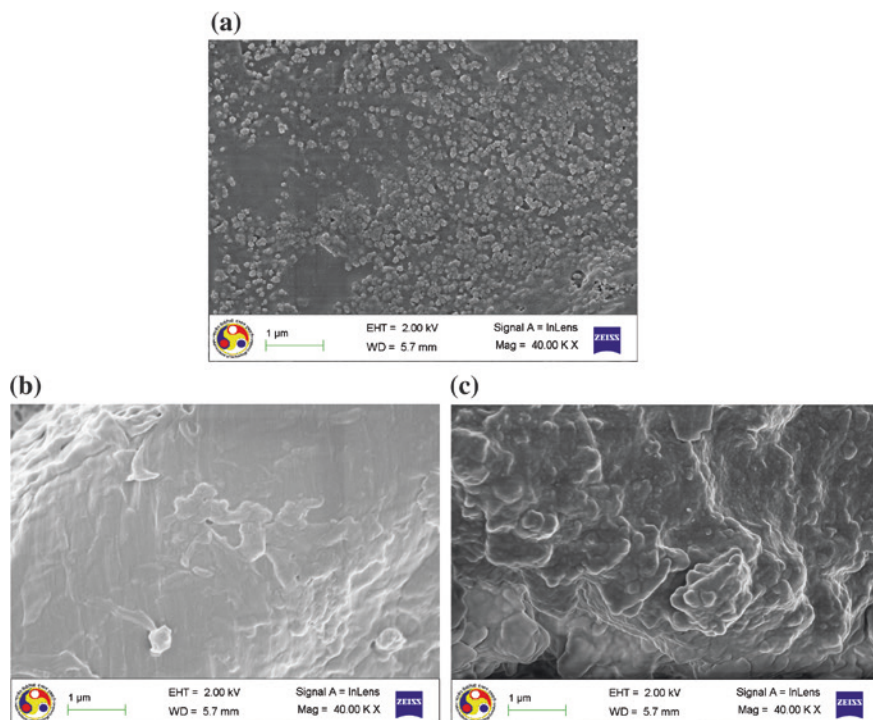


Fig. 2.11 FESEM micrographs of *P. hystrophorus* biomass **a** original biomass, **b** delignified biomass with mechanical agitation, and **c** delignified biomass with ultrasound. Reprinted with permission from [87], Copyright © 2014, American Chemical Society

and mechanical effects of cavitation bubbles are known to reduce with temperature. The kinetics of enzymatic hydrolysis was found to increase 18-fold with ultrasound. To obtain mechanistic insight into ultrasound induced enhancement, experiments were carried out with varying substrate concentration and the reaction kinetics was analyzed using Michaelis–Menten Model and Lineweaver–Burk plots. The values of $V_{\max}$ (reaction velocity) and K_m (substrate affinity constant) were compared for mechanical shaking and sonication. The value of reaction velocity showed an 18-fold increase, while the value of K_m stayed practically same with sonication. This result suggested that the enhancement effect of ultrasound on hydrolysis is in terms of increase in the reaction rate or velocity, which in turn could be a consequence of enhancement in convection in the medium that eliminates mass transfer, and increases the accessibility of substrate for the enzyme. The enzyme-substrate affinity, however, is an intrinsic property, which does not show any beneficial influence of ultrasound.

2.5 Conclusions and Future Outlook

In the preceding sections, we have put forth results of mechanistic investigations of several ultrasound assisted biofuels processes. A concurrent analysis of all of these results provides a coherent framework of the physics of ultrasound-induced enhancement. The physical effect of generation of strong micro-convection by ultrasound and transient cavitation seems to contribute to enhancement more than the chemical effect of radical generation. The technique of application of elevated static pressure provides a simple method for distinguishing between effects of ultrasound and cavitation. Among the individual contributions of ultrasound and transient cavitation, the physical effect of micro-streaming, i.e. rapid oscillatory motion of fluid elements is revealed to make greater impact than the microturbulence and shock waves generated by the transient cavitation. In some processes, such as oxidative desulfurization, transient cavitation is found to influence the system adversely. There are several reasons for some of the opposing trends that contribute to the overall effect of ultrasound on a reaction. In the first place, all biofuel systems are limited by the intrinsic characteristics of the system, which dominate the overall outcome of the process, and these intrinsic factors are relatively uninfluenced by physical and chemical effects of ultrasound. In addition, many chemical reactions actually occur in the bulk liquid and are catalyzed by ions, for example, methoxy radicals in transesterification and protons/hydroxyl ions in acid hydrolysis/delignification of biomass. Thus, the radicals generated by cavitation bubbles have no direct role in the reaction chemistry. In many systems, organic liquids are used as the liquid medium, for example, n-hexane or methanol/chloroform mixture for microalgal lipid extraction, or methanol for transesterification or toluene/n-hexane for oxidative desulfurization, which do not have intense transient radial motion of cavitation bubbles as in the case of when water is the reaction solvent. Accordingly, the physical and chemical effects induced by these bubbles are also not as intense as in water. This effect is attributed to the physical properties of the medium, i.e. large vapor pressure, low surface tension and low density. In addition, many secondary factors come into picture such as the probability of substrate-radical interaction. This factor is more pronounced for dilute systems such as extraction of lipids from microalgae. For microbial/enzymatic system, the transient cavitation has a sharp adverse effect in terms of the shock waves. These waves can cause disruption of microbial cells or denaturing of the enzymes. To understand the beneficial effects of ultrasound on chemical and biological systems, it is essential to isolate the effect of transient cavitation by application of elevated static pressure. An alternate solution is to keep the duty cycle of ultrasound irradiation sufficiently small so as to avoid continuous exposure of the microbial cells to ultrasound. However, the shock waves from transient cavitation have beneficial effects in case of heterogeneous reaction systems—examples of which are the liquid–liquid biphasic transesterification system or the solid–liquid delignification system. The heterogeneous systems have high mass transfer limitations, and thus, interphase transport is a dominant governing factor for kinetics as well as the

yield of these systems. Most of the biofuels systems described in this chapter have these limitations. The strong convection generated by ultrasound/cavitation helps overcome this mass transfer barrier, which helps in boosting the kinetics/yield of such systems. Fine emulsification generated by shock waves gives high interfacial area that boosts the kinetics of the process. Similarly, highly energetic collisions between biomass particles lead to breakage of lignin–hemicellulose bonds and also cause depolymerization of lignin.

Although, our studies have helped identify the physical mechanism of several biofuels system, one important facet of this system that has emerged from all results is the role of intrinsic characteristics of the system. These characteristics play a decisive role and place a limit on the ultrasonic enhancement of the process. For example, in case of microalgal lipid extraction, the selectivity of solvent is an intrinsic parameter. For acid catalyzed biodiesel synthesis, the intrinsic reactivity of the nucleophile attacking protonated carbonyl carbon is an intrinsic parameter. For oxidative desulfurization, diffusivity of PTA-oxidant complex is an intrinsic parameter. For an effective use of ultrasound energy input to the biofuels system, it is utmost essential that these intrinsic parameters be identified and studied in greater detail—as they form the limiting step of the process.

The results and analysis presented in this chapter give a typical framework for discerning the mechanistic issues of the biofuels system, which could be applied to many other biofuels systems not covered in this chapter. We believe that the review of research in physical mechanism of the ultrasound enhanced biofuels system will shed important light on the intricacies of these processes and will give crucial inputs for further research in this area.

References

1. Suslick KS (1990) Sonochemistry. *Science* 247:1439–1445
2. Hart EJ, Henglein A (1985) Free radical and free atom reactions in the sonolysis of aqueous iodide and formate solutions. *J Phys Chem* 89(20):4342–4347
3. Hart EJ, Henglein A (1987) Sonochemistry of aqueous solutions: hydrogen-oxygen combustion in cavitation bubbles. *J Phys Chem* 91:3654–3656
4. Luo J, Fang Z, Smith RL Jr (2014) Ultrasound-enhanced conversion of biomass to biofuels. *Prog Energ Combust Sci* 41:56–93
5. Morse PM, Ingard KU (1986) *Theoretical acoustics*. Princeton University Press, Princeton
6. Pierce AD (1989) *Acoustics: an introduction to its physical principles and applications*. Acoustical Society of America, New York
7. Suslick KS (1988) *Ultrasound: its physical, chemical and biological effects*. VCH, New York
8. Ensminger D (1988) *Ultrasonics: fundamentals, technology, applications*. Marcel Dekker, New York
9. Young FR (1989) *Cavitation*. McGraw Hill, London
10. Leighton TG (1994) *The acoustic bubble*. Academic Press, San Diego
11. Mason TJ, Lorimer JP (2002) *Applied sonochemistry: the uses of power ultrasound in chemistry and processing*. Wiley-VCH, Coventry
12. Shah YT, Pandit AB, Moholkar VS (1999) *Cavitation reaction engineering*. Plenum Press, New York

13. Flynn HG (1964) Physics of acoustic cavitation in liquids. In: Mason WP (ed) Physical acoustics. Academic Press, New York, pp 57–172
14. Brenner M, Hilgenfeldt S, Lohse D (2002) Single-bubble sonoluminescence. *Rev Mod Phys* 74:425–484
15. Neppiras EA (1980) Acoustic cavitation. *Phys Rep* 61:159–251
16. Plesset MS, Prosperetti A (1977) Bubble dynamics and cavitation. *Ann Rev Fluid Mech* 9:145–185
17. Thompson LH, Doraiswamy LK (1999) Sonochemistry: science and engineering. *Ind Eng Chem Res* 38(4):1215–1249
18. Adewuyi YG (2001) Sonochemistry: environmental science and engineering application. *Ind Eng Chem Res* 40:4681–4715
19. Atchley AA, Prosperetti A (1989) The crevice model of bubble nucleation. *J Acoust Soc Am* 86:1065–1084
20. Flynn HG (1975) Cavitation dynamics I. A mathematical formulation. *J Acoust Soc Am* 57:1379–1396
21. Rayleigh L (1917) On the pressure developed in a liquid during the collapse of spherical cavity. *Phil Mag* 34:94–98
22. Plesset MS (1949) Dynamics of cavitation bubbles. *J Appl Mech (Trans ASME)* 16:277–282
23. Poritsky H (1952) The collapse or growth of a spherical bubble or cavity in a viscous fluid. In: Sternberg E (ed) Proceedings of the 1st US national congress on applied mechanics, pp 813–821
24. Noltingk BE, Neppiras EA (1950) Cavitation produced by ultrasonics. *Proc Phys Soc* B63:674–685
25. Gilmore FR (1954) Hydrodynamic laboratory report, 26–4. California Institute of Technology, Pasadena
26. Kirkwood JG, Bethe HA (1942) The pressure wave produced by an under water explosion. Office of Science Research and Development, Report 558
27. Keller JB, Kolodner II (1956) Damping of underwater explosion bubble oscillations. *J Appl Phys* 27:1152–1161
28. Keller JB, Miksis MJ (1980) Bubble oscillations of large amplitude. *J Acoust Soc Am* 68:628–633
29. Prosperetti A, Lezzi A (1986) Bubble dynamics in a compressible liquid. Part 1. First order theory. *J Fluid Mech* 168:457–477
30. Brennen CE (1995) Cavitation and bubble dynamics. Oxford University Press, Oxford
31. Lofstedt R, Weninger K, Puttermann SJ, Barber BP (1995) Sonoluminescing bubbles and mass diffusion. *Phys Rev E* 51:4400–4410
32. Barber BP, Hiller RA, Lofstedt R, Putterman SJ, Weninger KR (1997) Defining the unknowns of sonoluminescence. *Phys Rep* 281:65–143
33. Colussi AJ, Weavers LK, Hoffmann MR (1998) Chemical bubble dynamics and quantitative sonochemistry. *J Phys Chem A* 102(35):6927–6934
34. Colussi AJ, Hoffmann MR (1999) Vapor supersaturation in collapsing bubbles: relevance to mechanisms of sonochemistry and sonoluminescence. *J Phys Chem A* 103:11336–11339
35. Kamath V, Prosperetti A, Egolfopoulos FN (1993) A theoretical study of sonoluminescence. *J Acoust Soc Am* 94:248–260
36. Prasad Naidu DV, Rajan R, Kumar R, Gandhi KS, Arakeri VH, Chandrasekaran S (1994) Modeling of a batch sonochemical reactor. *Chem Eng Sci* 49(6):877–888
37. Gong C, Hart DP (1998) Ultrasound induced cavitation and sonochemical yields. *J Acoust Soc Am* 104:2675–2682
38. Sochard S, Wilhelm AM, Delmas H (1997) Modeling of free radicals production in a collapsing gas-vapor bubble. *Ultrason Sonochem* 4:77–84
39. Moss WC, Young DA, Harte JA, Levalin JL, Rozsnyai BF, Zimmerman GB, Zimmerman IH (1999) Computed optical emissions from sonoluminescing bubbles. *Phys Rev E* 59:2986–2992

40. Yasui K (1997) Alternative model for single-bubble sonoluminescence. *Phys Rev E* 56:6750–6760
41. Yasui K (1997) Chemical reactions in a sonoluminescing bubble. *J Phys Soc Japan* 66:2911–2920
42. Krishnan SJ, Dwivedi P, Moholkar VS (2006) Numerical investigation into the chemistry induced by hydrodynamic cavitation. *Ind Eng Chem Res* 45:1493–1504
43. Storey BD, Szeri AJ (2000) Water vapor, sonoluminescence and sonochemistry. *Proc R Soc Lond Ser A* 456:1685–1709
44. Eames IW, Marr NJ, Sabir H (1997) The evaporation coefficient of water: a review. *Int J Heat Mass Transfer* 40:2963–2973
45. Storey BD, Szeri AJ (2001) A reduced model of cavitation physics for use in sonochemistry. *Proc R Soc Lond Ser A* 457:1685–1700
46. Toegel R, Gompf B, Pecha R, Lohse D (2000) Does water vapor prevent upscaling sonoluminescence? *Phys Rev Lett* 85:3165–3168
47. Hilgenfeldt S, Lohse D, Brenner MP (1996) Phase diagrams for sonoluminescing bubbles. *Phys Fluids* 8(11):2808–2826
48. Toegel R (2002) Reaction diffusion kinetics of a single sonoluminescing bubble. PhD dissertation, University of Twente, Netherlands
49. Hirschfelder JO, Curtiss CF, Bird RB (1954) *Molecular theory of gases and liquids*. Wiley, New York
50. Reid RC, Prausnitz JM, Poling BE (1987) *Properties of gases and liquids*. McGraw Hill, New York
51. Davis SL, Vibrational modes of methanol. (<http://classweb.gmu.edu/sdavis/research/modes.htm>)
52. Condon EU, Odishaw H (1958) *Handbook of physics*. McGraw Hill, New York
53. Crank J (1975) *The mathematics of diffusion*. Clarendon Press, Oxford
54. Press WH, Teukolsky SA, Flannery BP, Vetterling WT (1992) *Numerical recipes*, 2nd edn. Cambridge University Press, New York
55. Apfel RE (1981). In: Edmonds PD (ed) *Methods in experimental physics*, vol 19. Academic Press, New York, pp 355–413
56. Holland CK, Apfel RE (1989) An improved theory for prediction of microcavitation thresholds. *IEEE Trans Ultrason Ferroelectr Freq Control* 36:204–208
57. Nyborg WL (1958) Acoustic streaming near a boundary. *J Acoust Soc Am* 30:329–339
58. Kolb J, Nyborg WL (1956) Small scale acoustic streaming in liquids. *J Acoust Soc Am* 28:1237–1242
59. Lauterborn W, Hentschel W (1985) Cavitation bubble dynamics studied by high speed photography and holography: part one. *Ultrasonics* 23:260–268
60. Lauterborn W, Hentschel W (1986) Cavitation bubble dynamics studied by high speed photography and holography: part two. *Ultrasonics* 24:59–65
61. Pecha R, Gompf B (2000) Microimplosions: cavitation collapse and shock wave emission on a nanosecond time scale. *Phys Rev Lett* 84:1328–1330
62. Plesset MS, Chapman RB (1971) Collapse of an initially spherical vapour cavity in the neighbourhood of a solid boundary. *J Fluid Mech* 47:283–290
63. Blake JR, Taib BB, Doherty G (1986) Transient cavities near boundaries. Part I. Rigid boundary. *J Fluid Mech* 170:479–497
64. Blake JR, Taib BB, Doherty G (1987) Transient cavities near boundaries. Part II. Free surface. *J Fluid Mech* 181:197–212
65. Vogel A, Lauterborn W, Timm R (1989) Optical and acoustic investigations of the dynamics of laser-produced cavitation bubbles near a solid boundary. *J Fluid Mech* 206:299–338
66. Phillip A, Lauterborn W (1998) Cavitation erosion by single laser-produced bubbles. *J Fluid Mech* 361:75–116
67. Ilyichev VI, Koretz VL, Melnikov NP (1989) Spectral characteristics of acoustic cavitation. *Ultrasonics* 27:357–361

68. Moholkar VS, Warmoeskerken MMCG, Ohl CD, Prosperetti A (2004) The mechanism of mass transfer enhancement in textile with ultrasound. *AIChE J* 50:58–64
69. Ranjan A, Patil C, Moholkar VS (2010) Mechanistic assessment of microalgal lipid extraction. *Ind Eng Chem Res* 49:2979–2985
70. Kalva A, Sivasankar T, Moholkar VS (2009) Physical mechanism of ultrasound-assisted synthesis of biodiesel. *Ind Eng Chem Res* 48:534–544
71. Parkar PA, Choudhary HA, Moholkar VS (2012) Mechanistic and kinetic investigations in ultrasound assisted acid catalyzed biodiesel synthesis. *Chem Eng J* 187:248–260
72. Choudhury HA, Chakma S, Moholkar VS (2014) Mechanistic insight into sonochemical biodiesel synthesis using heterogeneous base catalyst. *Ultrason Sonochem* 21:169–181
73. Choudhury HA, Malani RS, Moholkar VS (2013) Acid catalyzed biodiesel synthesis from *Jatropha* oil: mechanistic aspects of ultrasonic intensification. *Chem Eng J* 231:262–272
74. Choudhury HA, Goswami PP, Malani RS, Moholkar VS (2014) Ultrasonic biodiesel synthesis from crude *Jatropha curcas* oil with heterogeneous base catalyst: mechanistic insight and statistical optimization. *Ultrason Sonochem* 21:1050–1064
75. Choudhury HA, Srivastava P, Moholkar VS (2014) Single-step ultrasonic synthesis of biodiesel from crude *Jatropha curcas* oil. *AIChE J* 60:1572–1581
76. Khanna S, Goyal A, Moholkar VS (2012) Bioconversion of biodiesel derived crude glycerol by immobilized *Clostridium pasteurianum*: effect of temperature. *Int J Chem Biol Eng* 6:301–304
77. Khanna S, Goyal A, Moholkar VS (2013) Effect of fermentation parameters on bio-alcohols production from glycerol using immobilized *Clostridium pasteurianum*: an optimization study. *Prep Biochem Biotechnol* 43:828–847
78. Khanna S, Ranjan A, Goyal A, Moholkar VS (2013) Medium optimization for mixed alcohols production by glycerol utilizing immobilized *Clostridium pasteurianum* MTCC 116. *Chem Biochem Eng Qtr* 27(3):319–325
79. Khanna S, Jaiswal S, Goyal A, Moholkar VS (2012) Ultrasound enhanced bioconversion of glycerol by *Clostridium pasteurianum*: a mechanistic investigation. *Chem Eng J* 200–202:416–425
80. Haldane J (1930) *Enzymes*. Longmans Green and Co., New York
81. Khanna S, Goyal A, Moholkar VS (2013) Mechanistic investigation of ultrasonic enhancement of glycerol bioconversion by immobilized *Clostridium pasteurianum* on silica support. *Biotechnol Bioeng* 110:1637–1645
82. Bolla MK, Choudhury HA, Moholkar VS (2012) Mechanistic features of ultrasound-assisted oxidative desulfurization of liquid fuels. *Ind Eng Chem Res* 51:9705–9712
83. Bhasarkar JB, Chakma S, Moholkar VS (2013) Mechanistic features of oxidative desulfurization using sono-Fenton–peracetic acid (ultrasound/ Fe^{2+} – CH_3COOH – H_2O_2) system. *Ind Eng Chem Res* 52:9038–9047
84. Bhasarkar JB, Chakma S, Moholkar VS (2014) Investigations in physical mechanism of the oxidative desulfurization process assisted simultaneously by phase transfer agent and ultrasound (communicated)
85. Suresh K, Ranjan A, Singh S, Moholkar VS (2014) Mechanistic investigations in sono-hybrid techniques for rice straw pretreatment. *Ultrason Sonochem* 21:200–207
86. Jacobsen SE, Wyman CE (2000) Cellulose and hemicellulose hydrolysis models for application to current and novel pretreatment processes. *Appl Biochem Biotechnol* 84–86:81–96
87. Singh S, Bharadwaja STP, Yadav P, Moholkar VS (2014) Mechanistic investigation in ultrasound-assisted (alkaline) delignification of *Parthenium hysterophorus* biomass. *Ind Eng Chem Res*. doi:10.1021/ie502339q
88. TAPPI (1992) Technical association of pulp and paper industry. Atlanta, Georgia, USA
89. STP Bharadwaja (2014) Mechanistic investigation in ultrasound assisted delignification and enzymatic hydrolysis of *Parthenium hysterophorus* for bioethanol production. M Tech dissertation, Indian Institute of Technology Guwahati, India

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