Fuel 184 (2016) 637–647

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Mathematical analysis of the effects of operating conditions and rheological behaviour of reaction medium on biodiesel synthesis under ultrasound irradiation

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A R T I C L E I N F O

Article history:
Received 11 February 2016
Received in revised form 23 June 2016
Accepted 24 June 2016
Available online 25 July 2016

Keywords:
Biodiesel
Ultrasound
Transesterification
Rheology
Micro bubbles
Mathematical modelling

A B S T R A C T

Ultrasound assisted transesterification has recently been introduced as an effective technology for biodiesel synthesis. However, the behaviour of micro bubbles under ultrasound is affected by operating conditions or rheological properties of reaction mixtures. This paper aims at investigating the changes of micro bubbles characteristics when operating conditions or rheological behaviour of the reaction medium are altered. The mechanistic simulation of micro bubbles was combined with the CFD simulation of reaction mixture to achieve the aims of this work. Continuity and momentum equations of Keller-Miksis model were employed along with reaction, mass and energy balances to simulate different characteristics of micro bubbles such as temperature, pressure, oscillation velocity, maximum radius of micro bubble, equilibrium state of bubble content, diffusion rates of reaction compounds towards bubbles and reaction within bubbles. It was found that among different combinations of reaction temperature, reactants ratio and intensity of ultrasound irradiation, the last one played the most important role. Radius, internal temperature and pressure of bubbles significantly increased with power amplitude due to stronger expansion and greater energy accumulation. At the same time, increase in reaction temperature and alcohol concentration made the bubbles characteristics rather moderate. It was also found that the growth of bubbles radius was reduced by about 4 times as the reaction progressed and the reaction mixture became more viscous and dense. The maximum internal temperature and pressure decreased by about 178 K and 220 bar due to moderate expansion of bubbles. Oscillation velocity was also restricted in this situation.

1. Introduction

Ultrasound technology, a technology which boasts energy efficiency, time and product quality can be used to introduce sufficient and uniform spatial energy into a system. This technology has been successfully employed in different processes such as leaching, degradation of recalcitrant pollutants, textile dyeing, waste treatment, chemical or biochemical process, etc. [1]. One of the main effects of ultrasound energy is generation of jet-like acoustic streaming which denotes the high-speed fluid flow generated by ultrasound energy, which exerts an impinging force on the liquid media and pushes it to move. This type of fluid flow that starts from an ultrasound probe is similar to a turbulent jet of fluid from a pipe of the same diameter [2]. The other important effect of ultrasound energy on its surrounding is generation, growth and transient collapse of micro bubbles that create intense local energy. Based on the theory, bubbles can reach extremely high temperature and pressure (500–15,000 K and 100–5000 bar respectively) at the moment of compression or collapse. Subsequently, superheated/highly pressurized regions which are also known as "hot-spots" are created. Growth and transient collapse of micro bubbles also causes formation of micro-streams, micro-turbulent eddies and shock waves. Small oscillatory motion of fluid elements in liquid bulk due to ultrasound irradiation is known as micro-streaming. Velocity of micro-streaming is defined by $v = P_A/\rho c$, where P_A, ρ and c denote amplitude of ultrasound pressure, bulk density and sound velocity within the medium. Liquid is displaced and pulled towards bubbles during the expansion phase. This oscillatory motion of liquid within its vicinity is known as micro-turbulence. The amplitude of bubble oscillation determines the micro-turbulence velocity [3]. Besides, bubbles (containing

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http://dx.doi.org/10.1016/j.fuel.2016.06.120

Nomenclature

c	sound speed	R	bubble radius
$C_{\upsilon,mix}$	specific heat	T_0	temperature of bubble wall
D	binary diffusion coefficient	T	temperature of bubble contents
E	activation energy	u	liquid velocity
f	ultrasound frequency	U_s	internal energy
H	enthalpy	V	bubble volume
h	van der Waals hard-core radius	X	mass fraction
h_s	molecular enthalpy	χ	thermal diffusivity
I	ultrasound intensity	α	mole fraction
k	Boltzmann constant	β	attenuation (absorption) coefficient
κ	thermal conductivity	ρ	liquid bulk density
l_{th}	thermal diffusion thickness	η	viscosity
M	molecular weight	ξ	liquid bulk viscosity
n	concentration	σ	surface tension
N_{tot}	total number of molecules	θ	vibrational temperatures
p	pressure (as specified by an equation of state)	υ	molar volume of species at its normal boiling temperature
$P(t)$	sinusoidal acoustic pressure	Φ_{MeOH}	association factor of methanol
p_g	gas pressure inside the bubble		
P_0	static pressure		

non-condensable gas) come to a sudden halt and rebound with high velocity at the maximum compression level, reflecting the converging fluid element from the wall. This process creates high-pressure shock waves. As a result, a fine micro emulsion that improves mass and heat transfer is generated. Such effects increase the overall volumetric efficiency, overcome mass transfer restrictions, accelerate chemical reaction, eliminate a number of steps in a multistep chemical synthesis or switch the reaction pathway.

Ultrasound has also been proven useful for biodiesel synthesis. Biodiesel is traditionally produced by transesterification of triglycerides such as edible/non-edible vegetable oils or animal fats with a short-chain-alcohol in catalytic or non-catalytic systems [4]. Transesterification is a three-step reversible reaction that starts with conversion of triglyceride to diglyceride and finally monoglyceride. Monoglyceride is then converted to glycerol. One molecule of methyl ester is produced in each step. Poor mass transfer due to immiscible nature of reactants is the key drawback of transesterification as it affects reaction yield. Numerous studies have been conducted to reduce or eliminate this problem through different approaches, which include optimization of operating parameters or use of a wide range of catalysts under ultrasound irradiation [5–8]. However, only a few studies have focused on mechanistic behaviour of micro bubbles and their effects on biodiesel synthesis. It should be noted that organic liquids and water generate different micro bubbles due to difference in their physical properties. For example, Moshaii et al. [9] discovered the damping role of bulk viscosity in non-linear bubble dynamics which influenced the rebounding amplitude of bubbles after the collapse. Some authors have also reported that micro bubbles under lower vapour pressures achieve higher temperatures at the moment of compression [10,11]. Choudhury et al. [12] modelled micro bubbles and their related phenomena during heterogeneous synthesis of biodiesel by using the diffusion limited ordinary differential equation model (ODE) with boundary layer approximation proposed by Toegel et al. [13]. The results indicated that there was no formation of any radical species from the micro bubbles. Hence, the authors employed a new version of classical Rayleigh–Plesset equation [14] which had been integrated with compressibility effects in their most recent work [15]. Besides, they employed Chapman–Enskog's theory using Lennard–Jones 12–6 potential to take into account heat and mass transfer. However, the authors only considered the compressibility of liquid motion around the bubbles. Besides, the bubble dynamics were studied in pure methanol in their study.

The impact of micro bubbles, their characteristics and total volume fraction and also the impact of acoustic jet-like streaming and its propagation in a liquid medium in a macro-scale sonoreactor were studied in the authors' previous works [16,17]. The authors then focused on the application of these phenomena, particularly micro-bubbles, in biodiesel synthesis process under low frequency/high power ultrasound irradiation (24 kHz, 300–400 W). Accordingly, a lone micro bubble was mechanistically simulated through mathematical modelling. The Keller-Miksis equation was employed for evaluating the bubble dynamic together with heat, mass and energy balances within the bubble. The objective was to identify the physical mechanism of cavitation and provide a deep insight into the ultrasound-assisted transesterification that form conditions that may activate the thermal decomposition phenomena and influence the biodiesel characteristics [18]. In continuation of the previous works, the current study follows two different but relevant objectives. (i) Identifying the effects of different operational conditions i.e. temperature, alcohol concentration and ultrasound power; on micro bubbles characteristics. (ii) Identifying the effect of reaction time and rheological properties of reaction medium on micro bubbles. Since, the volume fraction of biodiesel and glycerol increases as the reaction time goes on which affects the viscosity of the reaction system and the micro bubbles behaviour. Previous mathematical simulation was used except that at the rheological segment, the study was conducted by integrating the CFD simulation of the reaction mixture into the mathematical modelling of micro bubbles. The details of the mathematical modelling (which are summarised in Table 1) and the experimental analysis for better understanding can be found in the authors' previous work [18]. It should also be noted that, although the molar ratio of methanol to oil changed in some of the studied cases, their total volume was kept constant. In other words, a fixed volume of initial reaction mixture (total amount of oil and methanol) was used for all analysis in current and previous studies. Therefore, the ultrasonic energy per unit mixture solution volume did not change and the value of ultrasonic energy per unit of solution volume was only affected by the input power.