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Review article

State of the art review on development of ultrasound-assisted catalytic transesterification process for biodiesel production

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ABSTRACT

Excessive utilization of petroleum diesel has led to severe environmental pollution. Biodiesel, which is greener and renewable, can be a potential alternative fuel. Biodiesel is produced through transesterification reaction between vegetable oil, animal fat or even waste cooking oil (WCO) and alcohol in the presence of catalyst. Under process intensification, ultrasonic irradiation is employed in the transesterification reaction to enhance the agitation between immiscible reactants. Besides providing intensive mixing, it also offers uniform heating due to the localized temperature increase and formation of micro jets from the transient collapse of cavitation bubbles, thus reducing the energy consumption. The focus of this paper is to review the recent research progress on the ultrasound-assisted catalytic transesterification of non-edible vegetable oils using homogeneous and heterogeneous catalysts. The primary factors that affect the operation and efficiency of ultrasound-assisted transesterification such as alcohol to oil molar ratio, catalyst loading, reaction time, reaction temperature, energy consumption, phase separation time, ultrasonic pulse mode and biodiesel conversion or yield have been reviewed. The highlights of this review paper are the provisions on the mechanism of ultrasonic reactive extraction (RE) in the biodiesel production, kinetic study and the existing pilot reactors on the ultrasound-assisted transesterification which are still rarely reviewed in the current literature. Lastly, the challenges and feasibility for future development in the process intensification of biodiesel production are also addressed.

1. Introduction

Biodiesel is a liquid fuel which comprises of mono alkyl ester of long-chain fatty acid. In principle, it is a sustainable source of liquid transportation fuels as it is synthesized from various types of renewable lipids such as virgin vegetable oils, non-edible vegetable oils, waste vegetable oils (WVOs) and animal fats. Biodiesel can be produced from a variety of sources which include edible oils (e.g. canola, soybean, sunflower and palm oils), non-edible oils (e.g. *Jatropha curcas*, *Daturametel Linn, Hevea brasiliensis* and *Calophyllum inophyllum* oils), waste oils as well as animal fats (e.g. chicken fat, beef tallow and poultry fat) [1]. The increasing price volatility of fossil fuel has made biodiesel appears to have significant economic potential as a renewable fuel by lowering the dependency on crude oil foreign imports. Cheaper and non-edible feedstocks have been employed to produce biodiesel in order to alleviate the food crisis arising from the utilization of edible feedstocks [2,3].

Biodiesel has negligible sulphur and aromatics content with about 11% built-in oxygen content, which helps it to undergo complete combustion [4]. Therefore, it tends to produce less smoke and particles during combustion, resulting in lower emissions of harmful pollutants such as particulates, carbon monoxide (CO), unburned hydrocarbons (HCs) and sulphur oxides (SO_x) [5,6]. By employing biodiesel compared to diesel, the release of particulates, CO, unburned HCs and SO_x would be lowered by 40, 44, 68 and 100%, respectively [7]. In contrast, diesel fuel does not contain any oxygen element [8]. The sulphur content in the diesel fuel contributes to the formation of SO_x and sulphuric acid, which lead to acid rain. The aromatic compounds in the diesel fuel also increase particulate emissions and are considered carcinogens. Benzene, toluene, ethylbenzene, and o-, m-, p-xylene, popularly known as BTEX compounds, are well documented carcinogenic compounds emitted from the exhaust of a diesel-powered compression ignition (CI) engine [9]. Furthermore, biodiesel does not require any modifications when it is utilized in diesel engine directly due to its similar properties to diesel fuel, thus render it a suitable alternative to diesel fuel [10].

Transesterification is the most common process to synthesize biodiesel in the presence of alkali, acid or enzyme as catalyst. However, there are two major challenges encountered in the transesterification

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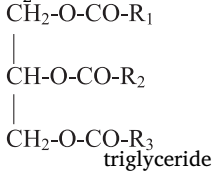
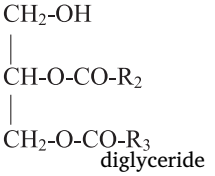
Nomenclature

R_1–COOH free fatty acid
NaOH sodium hydroxide
R_1COONa soap
H_2O water


triglyceride


diglyceride

CH_3OH methanol
R_1COOCH_3 fatty acid methyl ester
k reaction rate constant
X conversion of triglyceride at time,t
t time
C_{TG_0} molar concentration of triglyceride at time zero in mol/L

reaction. Firstly, heterogeneous nature of the reaction system poses challenges in mass transfer limitations. Secondly, higher alcohol to oil molar ratio is required because of the reversible nature of transesterification reaction. These result in higher operating cost and energy consumption which consequently lead to lower biodiesel production efficiency. There are several other transesterification techniques to produce biodiesel such as non-catalytic supercritical method, biox process, microwave, membrane technology, reactive distillation and ultrasonication. Non-catalytic supercritical method does not require catalyst, thus it does not face the disadvantages encountered in the catalytic routes such as the necessity of treating the free fatty acids (FFAs) and triglycerides (TGs) in different reaction stages, the inhibitory effects of water molecules present in the mixture, catalyst deactivation, separation of the catalyst from the product mixture, low glycerol purity, and generation of waste water. However, it is an energy intensive and economic infeasible process because it requires high operating temperature (553–673 K) and pressure (10–30 MPa) as well as high methanol-to-triglycerides molar ratio up to 42:1 [11]. For biox process, it employs co-solvents such as tetrahydrofuran (THF) to solubilize methanol for faster reaction. THF is commonly used due to its boiling point (339 K) is similar to methanol (337.7 K) which allows the removal of excess solvents in a single step once the reaction has completed [12,13]. This process is capable to convert oil feedstock containing high FFA content (more than 10%) into biodiesel and can be conducted under ambient temperature and pressure. However, economical barrier arises due to their close proximity of boiling point between methanol and co-solvent which makes the product separation to be very challenging [14]. In addition, complete removal of co-solvent from both the glycerol and biodiesel is compulsory due to its hazardous and toxicity natures [15,16]. Comparing to conventional transesterification, microwave method requires about 23 times lower energy consumption. This is because microwave energy is transmitted directly to the reactant, thus eliminating the preheating step. Furthermore, microwave process has more effective heat transfer system than conventional method. Conventional method transfers heat to the reaction via thermal heat reflux whereas microwave transfers energy in the form of electromagnetic wave [7]. Nonetheless, low penetration depth of microwave radiation into the absorbing materials limits the scaled-up to industrial scale [17]. On the other hand, membrane technology integrates reaction and separation into single step, thus minimizing separation costs and recycling requirements. However, membrane technology still requires further downstream purification since the fatty acid methyl ester (FAME)-rich phase will still contain methanol, glycerol and water [11,18]. For reactive distillation, it is advantageous for esterification process especially when dealing with high FFA feedstocks. Compared to the conventional method, it does not require excess alcohol due to the continuous removal of by-product (water) and is able to reduce the alcohol usage by 66% [11,19]. Even though reactive distillation process has less number of connections between instruments (due to smaller amount of equipment) which reduces the safety issues [20], the requirement for reboiler and condenser will increase the capital investment and operating costs tremendously [21]. Among the emerging transesterification techniques, ultrasonication appears to be a promising approach as it can enhance mixing, heat and mass transfer between different phases in alcoholysis process [22]. Consequently, it can reduce the operating cost and energy consumption as it has lower requirement on alcohol to oil molar ratio, catalyst amount and reaction time as well as no external heating requirement. In addition, phase separation of biodiesel from glycerol is simpler and shorter phase separation time is needed. Its superiority in transesterification reaction possesses a huge possibility to be scaled up from laboratory to industrial scale. However, it is noteworthy to consider also the problems associated with the utilization of biodiesel in engine. Biodiesel generally has 14–15% higher fuel consumption than diesel due to its lower calorific value (37.9 MJ/kg) than diesel (42.7 MJ/kg) while NO emissions are always 15–20% higher than diesel [23]. An overview of the advantages, disadvantages and recommendations of various emerging biodiesel production approaches is tabulated in Table 1.

This paper reviews in depth the ultrasound-assisted catalytic transesterification for biodiesel synthesis, effect of different parameters towards biodiesel conversion or yield in the ultrasound-assisted homogeneous and heterogeneous base-catalyzed transesterification as well as comparison between conventional stirring and ultrasonic cavitation in biodiesel production. In addition, this paper also provides fundamental understanding of ultrasonic mechanism and their effects on transesterification reaction. Most importantly, kinetic study on the ultrasound-assisted transesterification, latest pilot reactors for ultrasound-assisted biodiesel production and mechanism of ultrasonic reactive extraction on solid seed for biodiesel production are also reviewed in details.

2. Introduction of ultrasound

Ultrasound refers to sound wave above human audibility limit which is usually above 20 kHz [29]. It is categorized based on its frequency into high-frequency (2–10 MHz) and low-frequency (20–100 kHz) ultrasound [30]. Application of high-frequency operation is more effective for chemical synthesis and wastewater treatment as chemical effects induced are more intensive. Low-frequency operation is useful for enhancing the mass transfer across the immiscible reactants by increasing the interfacial surface area between them. Lower frequency is suggested to be employed for biodiesel synthesis since dominant physical effects are required for intensification of transesterification reaction [22]. High frequency will not benefit biodiesel synthesis because of the cavitation bubble collapses are weaker than impingement of the reactants [14]. Diverse forms of energy can be generated through ultrasonic applicator, which is shown in Fig. 1. An ultrasonic probe transforms electrical energy input into heat energy and vibrational energy. The vibrational energy is then transformed into cavitation energy while some of them is lost through sound reflection [13]. The cavitation energy is further converted into chemical, physical, and biological effects depending on the application and reaction