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Review

Biodiesel production in micro-reactors: A review

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ABSTRACT

In recent years, biodiesel, as a renewable and environment-friendly fuel has emerged as one of the most investigated bio-fuel with a goal to decrease our dependence on petroleum fuels and reduce environmental pollution. The current commercial technique of biodiesel production via transesterification is constrained by high operating cost and energy requirements, long residence time and limited conversion due to equilibrium limitations. On the other hand, the process intensification using the micro-reactor technology demonstrated an excellent performance ascribed to short diffusion distance and high surface area-to-volume ratio that can lead to high heat and mass transfer rates and improved mixing compared to the conventional reactors. This review provides an overview of the current status of biodiesel production in micro-reactors. It includes various types of micro-reactors used in the production of biodiesel, factors affecting the biodiesel production (i.e., temperature, residence time, alcohol to oil molar ratio, micro-channel size, inlet mixer type, internal geometries, co-solvent, catalyst type and concentration). This review also includes the factors affecting the liquid-liquid flow patterns and application of micro-reactor technology in the purification of biodiesel. Some of the critical observations from this review are, 1) inlet mixer type, channel size, and internal channel geometry (zig-zag, omega, and tesla shaped channels) have shown a significant effect on mixing in micro-channels. 2) In case of base-catalyzed transesterification, the biodiesel yield was found to increase up to the reaction temperature of 60–65 °C. 3) Homogeneous alkaline catalyst (NaOH, KOH, CH_3ONa) was preferred for the feedstock with low free fatty acid content (<1 wt%). However, an acid catalyst with high concentration, a significant amount of methanol and long reaction time were required for high free fatty acid feedstock (>1 wt%). Therefore, the current research is more focused on the investigation of heterogeneous catalysts in micro-reactors to develop an ecologically friendly process for the production of biodiesel. 4) Also, the reaction temperature and inlet mixer type had shown a significant effect on liquid-liquid flow patterns. This review also addressed the following literature gaps; a numbering-up technique to increase the throughput; catalyst development for high free fatty acid feedstock; continuous production of biodiesel in micro-reactors with in-line purification step to meet the energy demand and quality standards.

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Introduction

With the rapid depletion of fossil fuels and increasing environmental concerns, the need for an alternative fuel that is cheaper, renewable and environment-friendly is growing consistently. Biodiesel has emerged as a potential alternative fuel to fossil fuels, which has similar properties to fossil diesel with some advantages (Freedman, Pryde, & Mounts, 1984; Van Gerpen, 2005b). Biodiesel is a renewable fuel, less-toxic than conventional diesel and also biodegradable (Al-Zuhair, 2007; Bozbas, 2008; Knothe, Sharp, & Ryan, 2006; Koonin, 2006; Meher, Vidyasagar, & Naik, 2006). Biodiesel blends with conventional diesel up to B20 (20% biodiesel and 80% diesel) can be used in a diesel engine without engine modification. However, biodiesel >20% in the blend required few engine modifications (Canakci, Erdil, & Arcaklioğlu, 2006; Sharma, Singh, & Upadhyay, 2008; Van Gerpen, 2005a; Xue, Grift, & Hansen, 2011). Biodiesel is produced via transesterification of vegetable oils or fats with alcohol, typically methanol, in the presence of a catalyst (Demirbaş, 2003; Van Gerpen, 2005b). The transesterification reaction takes place in a liquid-liquid two-phase system and the reaction rate is limited by mass transfer due to immiscibility of oil and alcohol (Crawford et al., 2008; Guan, Kusakabe, Moriyama, & Sakurai, 2009a). Therefore, an efficient contact between the feed oil and the alcohol-catalyst mixture becomes crucial for achieving the high rate of reaction.

Several studies on biodiesel production were carried out using batch reactors (Dorado, Ballesteros, López, & Mittelbach, 2004; Lotero et al., 2005; Shah, Sharma, & Gupta, 2004; Vicente, Martınez, & Aracil, 2004; Xie, Peng, & Chen, 2006; Zhang, Dube, McLean, & Kates, 2003). These reactors were also commercially used for the production of biodiesel at industrial scale (Haas, McAloon, Yee, & Foglia, 2006). However, unfavourable economics and other design and operational issues at large-scale batch reactors pose challenges to the commercialization of biodiesel (Maddikeri, Pandit, & Gogate, 2012; Qiu, Zhao, & Weatherley, 2010; Santacesaria, Vicente, Di Serio, & Tesser, 2012). The critical challenges are, the long residence time of several hours, considerable investment in equipment and manufacturing floor space, high energy consumption and low production efficiency (Jachuck, Pherwani, & Gorton, 2009; Qiu et al., 2010; Slinn & Kendall, 2009; Warabi, Kusdiana, & Saka, 2004). On the other hand, with these limitations on a conventional batch process, several alternative highly energy efficient technologies to produce biodiesel in a continuous mode of operation were investigated (Maddikeri et al., 2012; Qiu et al., 2010). In recent years, micro-reactor technology has emerged as a promising technique for high-efficiency continuous biodiesel production (Xie, Zhang, & Xu, 2012). Micro-reactors are miniaturized reaction systems with reduced internal characteristic dimensions of 1000 μm–10 μm. Micro-reactors offer small diffusion distances and large surface area to volume ratio (10,000–50,000 $m^2\ m^{-3}$) and thus lead to high heat and mass transfer rates. As a result higher conversion is achieved in shorter residence time (Kashid & Kiwi-Minsker, 2009). Mixing time in micro-reactors is also considerably reduced due to their reduced internal dimensions. Moreover, small volume favours micro-reactors to perform highly exothermic reactions safely with precise control over the operating conditions (Benke, 2014; Burns & Ramshaw, 1999; Kobayashi, Mori, & Kobayashi, 2006). However, the production capacity of micro-reactors can be increased by the scale-out approach (Aran & Lammertink, 2013; Geyer & Seeberger, 2008).

Some researchers have successfully applied micro-reactors for biodiesel synthesis via transesterification (Aghel, Rahimi, Sepahvand, Alitabar, & Ghasempour, 2014; Buddoo, Siyakatshana, & Pongoma, 2008; Guan et al., 2009a; Martínez Arias, Fazzio Martins, Jardini Munhoz, Gutierrez-Rivera, & Maciel, 2012; Sun, Wang, Yao, Zhang, & Xu, 2009; Wen, Yu, Tu, Yan, & Dahlquist, 2009). It was demonstrated that as compared to conventional batch reactors, higher conversion in shorter residence time could be achieved in micro-reactors (Dai, Li, Zhao, & Xiu, 2014; Elkady, Zaatout, & Balbaa, 2015; Guan et al., 2009a; Martínez Arias et al., 2012; Rahimi, Aghel, Alitabar, Sepahvand, & Ghasempour, 2014; Santacesaria et al., 2012; Santana, Tortola, Reis, Silva, & Taranto, 2016; Schürer, Thiele, Wiborg, Ziogas, & Kolb, 2014; Sun, Ju, Ji, Zhang, & Xu, 2008). It should also be noted that as compared to conventional reactors, biodiesel could be produced 10 to 100 times faster in a micro-reactor. Moreover, the requirements of high energy in the mixing of reactants, ample floor space and standing time for the separation of products are eliminated using micro-reactors (Buddoo et al., 2008; Jovanovic, 2006). Although the amount of biodiesel produced using a single micro-reactor is a trickle, each unit can be numbered up to increase the throughput from lab to commercial scale (Billo et al., 2015; Jovanovic, 2006; Schürer et al., 2016). The process of transesterification in micro-reactors is observed to be affected by the operating conditions as well as the type and geometrical parameters of micro-reactor (Xie et al., 2012). With this background, the present review has been organized as following sections: 1) the present state of the art: the types of micro-reactors used in biodiesel synthesis with different feedstock have been discussed. 2) The factors affecting biodiesel production in micro-reactors, in which, the effect of operating parameters such as temperature, alcohol to oil molar ratio, the effect of co-solvent addition, catalyst type and concentration as well as the effect of the geometrical configuration of micro-reactors have been discussed. 3) Liquid-liquid two-phase flows in micro-reactors for biodiesel production: flow patterns observed during production of biodiesel and the factors affecting the flow patterns have been discussed. 4) Purification of biodiesel in micro-reactors: the current research techniques applied for biodiesel separation from glycerol at micro-scale are mentioned. Finally, the current research gaps that need further investigations into full-scale commercialization of biodiesel production using micro-reactors are also addressed.

Present state of the art: micro-reactors used in biodiesel synthesis

Micro-reactors can be categorized by geometries, fabrication material, and techniques. For the production of biodiesel, mainly micro-tubular and micro-channel reactors have been applied. In general, the micro-reactor system is composed of a mixer for intensifying mixing