Progress in Energy and Combustion Science 45 (2014) 54–78

Contents lists available at ScienceDirect

Progress in Energy and Combustion Science

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

Review

Integration of reactive extraction with supercritical fluids for process intensification of biodiesel production: Prospects and recent advances

Keat Teong Lee [a,*], Steven Lim [b], Yean Ling Pang [b], Hwai Chyuan Ong [b], Wen Tong Chong [b]

[a] School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia
[b] Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

ARTICLE INFO

Article history:
Received 16 April 2014
Accepted 6 May 2014
Available online 12 August 2014

Keywords:
Supercritical reactive extraction
Biodiesel
Bio-refinery
Process intensification
Product utilization
Biofuels

ABSTRACT

Current world energy usage is trying to gradually shift away from fossil fuels due to the concerns for the climate change and environmental pollutions. Liquid energy from renewable biomass is widely regarded as one of the greener alternatives to partially fulfil the ever-growing energy demand. Contemporary research and technology has been focussing on transforming these bio-resources into efficient liquid and gaseous fuels which are compatible with existing petrochemical energy infrastructure. Due to the wide range of properties and compositions from different types of biomass, there are ample of processing routes available to cater for different demands and requirements. In addition, they can produce multi-component products which can be further upgraded into higher value products. This conceives the idea of bio-refinery where different biomass conversion processes are incorporated and proceed simultaneously at one location. However, the underlying complexity in integrating different processes with varying process conditions will undoubtly incurs prohibitive cost. Consequently, process intensification plays an important role in minimizing both the capital and operating costs associated with process integration in bio-refineries. Recently, process intensification for biodiesel production has been developing rigorously due to increasing demand for cost-cutting measures. Supercritical fluid process allows biodiesel production to be performed without any addition of catalyst. Meanwhile, catalytic *in situ* or reactive extraction process for biodiesel production successfully combines the extraction and reaction phase together in a single processing unit. In this review, the important characteristics and recent progress on both of the intensification processes for biodiesel production will be critically analyzed. The prospects and recent advances of supercritical reactive extraction (SRE) process which integrates both of the processes will also be discussed. This review will also scrutinize on the methods for these processes to compliment future bio-refinery setup and more efficient utilizing of all of the products generated.

Contents

* Corresponding author. Tel.: +60 4 5996467; fax: +60 4 5941013.
E-mail address: ktlee@usm.my (K.T. Lee).

http://dx.doi.org/10.1016/j.pecs.2014.07.001
0360-1285/

1. Introduction

Energy supply and security is one of the most pressing issues shrouding our civilization development which remained to be tackled. For the past century, we have become over-reliant on fossil fuels to generate the energy we required for our technological and social development until neglecting the devastating effects they might bring to our ecosystem. However, the quest to replace fossil fuels to more sustainable energy sources remains sluggish especially in developing countries which account for more than two thirds of the world population. The slow transition from fossil fuels to alternative energy sources can be attributed to various factors such as low accessibility, high cost, insufficient infrastructure, inadequate technology and sub-par efficiency [1]. Among the renewable energy sources, biofuels from biomass such as biodiesel are currently recognized as one of the best alternatives to partially displace the usage of fossil fuels in the energy sector [2]. Biodiesel, which is usually derived from plant oils or animal fats, can be blended with mineral diesel up to 20% w/w (B20) and applied to existing combustion ignition engine without any modifications. Apart from that, it is also known to be biodegradable, low toxicity, lower emissions of harmful pollutants (CO, SO_x and unburned hydrocarbons), easy handling and distribution [3].

Despite these advantages, biodiesel advocates and developers still find it difficult to break into the energy market conventionally dominated by fossil fuels. Traditionally, biodiesel is produced using homogeneous basic catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) [2]. This production route demands a high purity oil feedstock which will otherwise reduce the process yield due to side-reactions such as saponification. In addition, homogeneous catalysts are usually difficult to be removed from the product stream and this will incur extra purification cost. In lieu with the shift from edible feedstocks to non-edible or waste feedstocks to avoid the food versus fuel ethical issue, other advanced biodiesel production methods have been explored intensively. In general, they can be categorized into three primary processes; the heterogeneous catalytic process, biological enzymatic process and supercritical fluids non-catalytic process. Each process has its own advantages and disadvantages while ample of research studies have been performed to further improve the processes in terms of the esters yield and cost-competitiveness.

In this context, process intensification has been lauded as having huge potential to improve biodiesel production process tremendously through various cost-effective measures. Process intensification can be generally defined as any engineering development of novel apparatus or technique which resulted in a substantially smaller, cleaner and more energy-efficient production technology [4]. Several process intensification measures proposed for biodiesel production include the novel oscillatory baffled reactor, heterogenization of the catalysis, supercritical non-catalytic reactions, reactive extraction process and ultrasound/microwave assisted process [5,6]. Reactive extraction or also known as *in situ* extraction combines the extraction and reaction processes together in a single unit operation. There are usually two routes for this to be done. Conventionally, biodiesel production from edible oils starts with the extraction of oil from the lipid-bearing solid material either through mechanical pressing or chemical extraction. The extracted liquid oil will then undergo several purification stages before subjected to transesterification process with short-chain alcohol to produce esters which are equivalent to biodiesel. The implementation of reactive extraction allows the elimination of pre-extraction step which can potentially reduce the operating cost and time [7]. The second type of reactive extraction deals with simultaneous removal of the glycerol from the ester phase during