Renewable and Sustainable Energy Reviews 49 (2015) 500–516

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

Purification of crude biodiesel obtained by heterogeneously-catalyzed transesterification

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ARTICLE INFO

Article history:
Received 3 April 2014
Received in revised form
11 November 2014
Accepted 23 April 2015

Keywords:
Biodiesel
Dry washing
Ion-exchange
Membrane extraction
Precipitation
Wet washing.

ABSTRACT

This review paper presents the methods that have been used to date for the purification of crude biodiesel obtained by heterogeneous production processes. At first, a typical biodiesel production process using heterogeneous catalysts is shortly described, paying attention to the main processing steps. Then, possible impurities and their effects on the biodiesel quality are pointed out. The main part of this review paper deals with the traditional (wet and dry washing) and novel (membrane extraction, precipitation, complexation, simultaneous ion-exchange and precipitation as well as simultaneous biodiesel synthesis and purification) purification methods. These purification methods are compared with respect of their refining efficiency. A special attention is paid to their comparison regarding the type of raw materials used in biodiesel production. Furthermore, advantages and disadvantages of the crude biodiesel purification methods are emphasized. Finally, environmental aspects of crude biodiesel purification are highlighted.

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1. Introduction

Biodiesel has gained world-wide attention in recent years as an alternative fuel that has a number of favorable properties such as

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http://dx.doi.org/10.1016/j.rser.2015.04.097
1364-0321/

Table 1
Comparison of homogeneous and heterogeneous catalysis for biodiesel production.[a]

Type of catalyst	Advantage	Disadvantages
Homogeneous	Modest reaction conditions	Separation problems after reaction and wastewater treatment
	High activity of base catalysts results in high yield in short time	Saponification forms stable emulsion
	Base catalysts are much more active than acid catalysts	Catalyst cannot be reused
	Methoxides are more effective than hydroxides	Basic catalysts are sensitive to the presence of FFA and water
	Acid catalysts can be used for esterification and transesterification	Higher process cost compared with heterogeneous processes
	Acid catalysts are insensitive to the presence of FFA and water	Acid catalysts give very slow reaction rate and are corrosive
		Acid catalysts require higher methanol-to-oil molar ratio and temperatures
Heterogeneous	Environmentally friendly, noncorrosive, recyclable and with fewer disposal problems	Currently less effective than common homogeneous base catalysts
	Easy separation of products, higher selectivity, longer catalyst life	Mass transfer limitations in the multi-phase reaction system
	Acid catalysts can be used for esterification and transesterification	Basic catalysts require oily feedstocks with low FFA and water content
	Acid catalysts are insensitive to the presence of FFA and water	High alcohol-to-oil molar ratio, temperature and pressure can be required
	Can be used in fixed-bed reactors with continuous operation	Higher cost of acid catalysts compared to basic catalysts
	Comparatively cheap	Possible leaching into the reaction mixture

[a] Adapted from Endalew et al. [6].

high degradability, no toxicity as well as low emission of carbon monoxide, particulate matters and unburned hydrocarbons. Biodiesel is a mixture of fatty acid alkyl esters and it can be used in conventional diesel engines, which need almost no modification. So far, it has mainly been produced by transesterification of triacylglycerols (TAGs) and/or esterification of free fatty acids (FFAs) from various natural sources like vegetable oils and animal fats or waste cooking oils using homogeneous basic (most frequently sodium or potassium hydroxide) or acid (sulfuric acid) catalysts, respectively that are usually dissolved in methanol. Because of high activity of traditional basic catalysts and mild reaction conditions, the conversion of TAGs into methyl esters completes within 1 h at atmospheric pressure and relatively temperature (up to 65 °C). However, these processes have several drawbacks such as soap formation, reduction of catalytic efficiency caused by the catalyst consumption, the increase in viscosity and the formation of gels. In addition, for wet washing of crude biodiesel, the most frequently used purification method, a large amount of water is needed in order to remove the residual catalyst and to clean the biodiesel product, thus producing a huge amount of wastewater that should be adequately treated. This additional step in the overall biodiesel production process increases the overall cost of the process, making it non-competitive to the diesel production from petroleum. The cost of biodiesel production is about 1.5–3 times more expensive than petroleum based diesel [1,2]. Furthermore, homogeneous catalysts cannot be reused, which is probably their major disadvantage. Finally, homogeneous base-catalyzed transesterification is limited by availability of refined oily feedstocks. Despite being readily available and inexpensive, non-refined feedstocks (crude oils, rendered animal fat and greases) have limited use in base-catalyzed transesterification because of high content of FFAs that unfavorably react with the base catalyst.

An alternative that could eliminate some drawbacks of traditional homogeneous base-catalyzed biodiesel production processes is the use of heterogeneous catalysts. First of all, heterogeneous can be used in batch reactors repeatedly or in continuous fixed-bed reactors. Moreover, the use of solid catalysts results most probably in simpler and cheaper separation processes, reduction of the wastewater effluent and capital and energy costs. For instance, solid catalysts could be retained in the reactor simply by filtration. Therefore, the operating costs associated with the additional separation and purification stages could be avoided. Furthermore, heterogeneous catalysts exhibit a less corrosive character and can be used in a fixed-bed reactor, leading to safer, cheaper and more environment-friendly operation [3]. The benefit with heterogeneous catalysts is their lower consumption in the transesterification reaction. For example, 88 t of NaOH is required to produce 8000 t of biodiesel, while only 5.6 t of supported MgO are sufficient to produce 100,000 t of biodiesel [4]. The disadvantages of solid catalyst are slow kinetics, incomplete conversions, severe conditions, limited lifetime and high costs [5]. At last, crude glycerol of higher purity could be obtained in heterogeneous reaction systems. The main disadvantage of solid catalysts, namely their lower reaction rate in comparison to the rate of homogeneous reactions, can be overcome by using higher methanol-to-oil ratios, temperatures and pressures. Therefore, the use of efficient heterogeneous catalysts opens up the possibility of more favorable processes for biodiesel production. Table 1 summarizes the advantages and disadvantages of homogeneous and heterogeneous catalysts for biodiesel production.

Both acids and bases are used as heterogeneous catalysts in transesterification and esterification reactions. Various types of solid catalysts have been assessed such as alkali earth oxides, alkali oxides, not metal oxides, metal oxides, cation exchange resins, metal phosphates and acid supported on different materials [4]. The chemical nature of solid catalysts determines the rate of transesterification reaction. The stronger basicity due to the presence of more active basic sites improves the catalytic activity in the transesterification reaction. Therefore, biodiesel is usually produced in the presence of a base catalyst, although acid catalysts have also been used. Despite all the efforts, heterogeneous catalysts for biodiesel production have not been widely exploited at industrial level, yet. So far, only a biodiesel production process using a mixed oxide of zinc and aluminum has been carried out commercially [7]. However, this technology is spreading to different parts of the world [6].

In order to be used the biodiesel produced in heterogeneously catalyzed processes must comply the prescribed biodiesel standard specifications such as EN 14214 or ASTM D6751. Hence, once produced, crude biodiesel (commonly a mixture of fatty acid methyl esters) should be purified. Various impurities, such as unconverted TAGs, mono- and diacylglycerols, FFAs, glycerol, water, catalyst, soaps and others must be removed from crude biodiesel by the downstream purification steps in order to prevent the damage of diesel engines [8]. Whereas the development and use of heterogeneous catalysts for biodiesel synthesis have widely been described in many publications, a little attention has been paid to the quality of biodiesel obtained in heterogeneous catalytic systems [9]. There are only a few studies concerning the purification of crude biodiesel obtained by processes using calcium oxide as the basic catalyst [10–13]. Since today's commercial production of biodiesel is based on homogeneous catalytic systems, it is not