Renewable and Sustainable Energy Reviews 47 (2015) 589–603

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

The potential of waste cooking oil-based biodiesel using heterogeneous catalyst derived from various calcined eggshells coupled with an emulsification technique: A review on the emission reduction and engine performance

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A R T I C L E I N F O

Article history:
Received 3 July 2014
Received in revised form
19 January 2015
Accepted 8 March 2015

Keywords:
Biodiesel
Emulsification
Transesterification
Solid base catalyst
Heterogeneous catalyst
Calcination
Eggshell

A B S T R A C T

Nowadays, biodiesel is an alternative fuel to replace the existing petroleum-based diesel. The advantages of biodiesel are good combustion efficiency, high-lubricity, biodegradability and low toxicity. Biodiesel can be an alternate fuel to be used for running diesel engines. This paper is to present a comprehensive review on the past efforts to enhance and commercially improve the transesterification by using homogeneous base catalyst, e.g. sodium hydroxide or potassium hydroxide. By introducing heterogeneous base catalyst such as calcium oxide which was made from waste material such as chicken eggshell, quail eggshell and ostrich eggshell it may cater the excessive washing problem to remove the excessive reactants and glycerol. It is also an environment friendly way of recycling the waste eggshells; nevertheless, the NO_x emission remains high – around 5–10% more than conventional diesel fuel. Thus, subsequently, this paper also discusses emulsification of biodiesel with water to investigate its influence on the overall diesel engine performance which includes a comparison study of gas emission from pure biodiesel, diesel and emulsion of biodiesel and water. Compared with conventional biodiesel, some of the notable advantages from this water emulsified biodiesel are the emission reduction of NO_x, particular matter, unburned hydrocarbon and carbon monoxide.

Contents

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http://dx.doi.org/10.1016/j.rser.2015.03.048
1364-0321/

1. Introduction

Biodiesel (Greek, bio, life + diesel from Rudolf Diesel) refers to a diesel-equivalent, processed fuel derived and ester-based oxygenated fuel from renewable biological sources [1]. It can be made from processed organic oils and fats such as soya bean, rapeseed, sunflower, coconut, corn, cottonseed, mustard, palm oil, peanut, animal fats, waste vegetable oil and algae.

In general terms, biodiesel may be defined as a domestic, renewable fuel for diesel engines which meet the requirements of ASTM D 6751. In technical terms (ASTM D 6751) biodiesel is a diesel fuel made of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated as B100 and meeting the specifications of ASTM D 6751 [2].

Chemically, biodiesel refers to the long-chain alkyl esters (monoalkyl esters, especially (mono)ethylester of long-chain fatty acids like lauric, palmitic, stearic, oleic, etc.) derived from renewable biological sources via a transesterification process. Table 1 shows the chemical properties of biodiesel.

Generally, biodiesel is produced through the chemical reaction by the transesterification process of a vegetable oil or animal fat with alcohol in the presence of catalyst, to obtain methyl or ethyl esters (biodiesel) and glycerin (soap, side product) [3]. Fatty acid (m)ethyl esters or biodiesels are produced from natural oils such as rapeseed oil, canola oil, soybean oil, sunflower oil, palm oil, waste cooking oils, and animal fats. Typically, chemical reagent methanol is more preferred for the transesterification process to produce biodiesel because its lower cost than ethanol [4].

Application wise, biodiesel can be used as an extender for combustion in CIEs (diesel engine); it reduces exhaust gas emissions [5]. Biodiesel can be used alone or mixed with any petrodiesel in any suitable ratio in standard diesel engines without any engine modification. Biodiesel is a good low carbon alternative fuel which has additional advantages such as better lubricant, biodegradability, combustion efficiency and low toxicity compared to the other fuels. Thus, biodiesel has many environmentally beneficial properties.

The process used to convert renewable biological source oils to biodiesel is called transesterification. The transesterification process is the chemical reaction of a triglyceride (fat/oil) with an alcohol (methanol/ethanol) in the presence of a sodium hydroxide or potassium hydroxide which acts as catalyst to form biodiesel, (m)ethyl esters, and glycerin [5].

Commercially biodiesel is produced by homogeneous transesterification reaction using methanol; the raw materials are fats, oil and homogeneous catalyst such as sodium hydroxide. This reaction is in homogenous stage with all reagents being in liquid stage. The homogeneous catalytic process has several disadvantages, i.e. producing a huge amount of wastewater for the purification end product process and the non-reusable homogeneous catalysts [7]. Heterogeneous catalyst is discovered as one of the good options to solve the problems stated above [8]. A heterogeneous catalytic process can be simplified by the purification product process by eliminating the neutralization step of producing waste water [9]. Besides that, the heterogeneous catalyst can be separated easily and probably be reusable. Hence, the capital cost is lower [10]. Heterogeneous base catalyst can be derived from waste sources such as bones, ashes, rocks and shells. These waste sources have high potential to function as biodiesel production catalysts. In this research, in order to get the calcium oxide, CaO catalyst naturally for the biodiesel production, eggshells from our daily waste is a good calcium resource. Also, the heterogeneous base catalyst, calcium oxide, CaO derived from waste eggshells was further explained with the results done by the previous researchers.

Nevertheless, due to the high oxygen content in B100 pure biodiesel has rise up the problem of higher NO_x emission. Lapuerta et al. [11] reported that burning of B100 would produce approximately 10% more NO_x than petroleum diesel because the oxygen content in biodiesel increases the formation of nitrogen oxide (NO_x). Monyem et al. [12] had further investigate the application of micro-emulsion of biodiesel with water in diesel engine which shows a reduction in carbon monoxide (CO), carbon dioxide (CO_2), unburned hydrocarbon (HC), particulate matter (PM) and NO_x when compared with using normal petrodiesel. In this research, a microemulsion technique is chosen as the best option to increase the performance of biodiesel in diesel engine and reduce the emission of greenhouse gases.

2. Biodiesel production

There are several methods for biodiesel production: direct use of vegetable oil, microemulsions, thermal cracking (pyrolysis), transesterification or esterification, ultrasonic reactor, microwave method, supercritical method and enzymatic method using lipase [13]. Direct use of raw vegetable oil in diesel engines is not feasible due to their characteristic of having high viscosity at room temperature and low volatilities than commercial diesel fuel which reduces fuel atomization, incomplete combustion and increases penetration. Incomplete combustion or failed ignition will lead to the carbon being deposited on to the injector, serious engine fouling [14] and piston ring sticking which would damage the diesel engine.

To get rid of the problems due to high viscosity of raw vegetable oils, several methods such as dilution (blending), micro-emulsification, pyrolysis (thermal cracking), transesterification, ultrasonic reactor, microwave method, supercritical method and enzymatic method using lipase are briefly explained as follows:

(i). *Dilution* (*blending*). Dilution is one of the easiest ways to reduce the viscosity of crude vegetable oils. It can be accomplished by direct blend or diluted with the conventional diesel fuel. While completely pure (100%) biodiesel is defined as B100, a biodiesel blend is pure biodiesel mixed with the conventional petro-based diesel. Dilution can improve the viscosity, overcome the engine performance problems such as injector coking and carbon deposition [14]. Nevertheless, dilution is not suitable for long term use in a direct injection engine due to higher viscosity, lower volatility and the reactivity of unsaturated hydrocarbon chains.

(ii). *Micro-emulsification*. Microemulsions are clear, colloidal equilibrium dispersion of isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a co-surfactant [15]. Depending on the continuous phase, the marcoemulsions are classified into dispersion of oil in water (O/W) or water in oil (W/O) [16]. While microemulsion is a