Renewable and Sustainable Energy Reviews 31 (2014) 446–471

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

Biodiesel from vegetable oils

Titipong Issariyakul, Ajay K. Dalai *

Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, SK, Canada S7N 5A9

ARTICLE INFO

Article history:
Received 8 September 2011
Received in revised form
16 October 2013
Accepted 9 November 2013
Available online 17 January 2014

Keywords:
Transesterification
Esterification
Hydrolysis
Homogeneous catalysts
Heterogeneous catalysts
Biodiesel
Vegetable oils

ABSTRACT

Biodiesel is gaining acceptance in the market as fuel and lubricant. It is expected that biodiesel industries will rapidly grow worldwide in the coming years and information on biodiesel feedstock, production, and characteristics will be crucial than ever especially for those using vegetable oils as feedstock as these are currently the major sources for making biodiesel. In the present paper, a comprehensive review is reported on feedstock, production technologies, and characteristics of biodiesel. More specifically, selected available vegetable oils are explored as feedstock for biodiesel production. Production technologies including latest catalyst developments are discussed. Finally, biodiesel characteristics and parameters influencing the corresponding properties are revealed. Since this paper covers a wide range in biodiesel area, it serves as a general public education medium as well as a research reference for biodiesel production from vegetable oils.

Contents

1. Introduction . . . 447
2. Feedstock . . . 447
   2.1. Soybean oil . . . 448
   2.2. Rapeseed oil, mustard oil, and canola oil . . . 449
   2.3. Palm oil . . . 450
   2.4. Sunflower oil . . . 450
   2.5. Rice bran oil . . . 450
   2.6. Jatropha oil . . . 450
   2.7. Karanja oil . . . 451
   2.8. Used cooking oil . . . 451
3. Biodiesel production . . . 451
   3.1. Effects of free fatty acid and water content . . . 452
   3.2. Effects of alcohol used in transesterification . . . 452
   3.3. Effects of catalyst type . . . 453
      3.3.1. Homogeneous base catalysis . . . 454
      3.3.2. Homogeneous acid catalysis . . . 455
      3.3.3. Heterogeneous base catalysis . . . 456
      3.3.4. Heterogeneous acid catalysis . . . 456
   3.4. Effects of reaction time, temperature, and the reaction kinetics . . . 459
   3.5. Techniques for monitoring transesterification . . . 460
      3.5.1. Gas chromatography . . . 460
      3.5.2. Liquid Chromatography . . . 461
      3.5.3. Nuclear magnetic resonance spectroscopy . . . 461
      3.5.4. Infrared spectrometry . . . 462

* Correspondence to: Department of Chemical and Biological Engineering, 57 Campus Drive, University of Saskatchewan, Saskatoon, SK, Canada S7N 5A9. Tel.: +1 306 966 4771; fax: +1 306 966 4777.
E-mail address: ajay.dalai@usask.ca (A.K. Dalai).

1364-0321/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.rser.2013.11.001

3.5.5. Other methods . . . 462
3.6. Post reaction treatment . . . 462
4. Biodiesel quality . . . 462
4.1. Burning properties . . . 462
4.2. Flow properties . . . 463
4.3. Stability . . . 464
4.4. Lubricity . . . 465
4.5. Minor components . . . 466
4.5.1. Pigments . . . 466
4.5.2. Lecithin and phospholipids . . . 466
4.5.3. Phytosterols . . . 466
4.5.4. Glycolipids . . . 467
5. Biodiesel production in Canada . . . 467
6. Conclusions . . . 468
Acknowledgment . . . 468
References . . . 468

1. Introduction

The depleting trend of conventional, non-renewable, fossil-based fuel has triggered research and development on alternative renewable energy. Biodiesel is one of the most promising renewable energy in this century. Recently, a 5.54 fossil energy ratio (FER) was reported [1] which means one unit of fossil energy input is required to produce 5.54 units of biodiesel energy output. This FER shows a stunning energy return of biodiesel that surpasses other fuels [2]. Furthermore, FER of biodiesel is expected to be increased even further in the coming years mainly due to increased crop yield, adoption of energy-saving farm practices, and continuous development of energy-efficiency technologies. In addition, biodiesel has many superior properties as compared to petroleum diesel such as lower exhaust emissions, biodegradable, non-toxic, renewable, and free of sulfur [3–5]. Since biodiesel is renewable and environmentally friendly, the use of this fuel is a shift towards sustainable energy.

The history of biodiesel is as long as that of diesel engine itself. The use of vegetable oils was investigated as early as the era when diesel engine was developed. Rudolf Diesel (1858–1913), the inventor of diesel engine, tested peanut oil as fuel for his engine. Many vegetable oils were investigated during "historic times" which includes palm oil, soybean oil, cottonseed oil, castor oil, etc. These early publications showed satisfactory performance of vegetable oil as fuel for diesel engine [6]. However, there were concerns that their higher costs as compared to petroleum fuel would prevent their prevalent uses. In spite of their performance in diesel engine, vegetable oils create engine problems when used as diesel fuel especially in direct-injection engines. The major drawback of vegetable oils is their high viscosity which causes coking and trumpet formation on the injectors resulting in poor atomization and ultimately leads to operational problems such as engine deposits [7]. Four possible solutions to reduce viscosity of vegetable oil were proposed: transesterification, pyrolysis, dilution with petroleum-based fuel, and emulsification [8]. Transesterification is the most common method which yields mono alkyl esters of long chain fatty acids or fatty acid alkyl ester (FAAE). This idea was originated back in 1938 that the glycerin part has no calorific value and is likely to cause excess carbon deposit on the engine and therefore should be eliminated from the vegetable oils. The engine should run on the residue fatty acid [9]. The residue fatty acid is what is today known as "biodiesel", although ester was not mentioned during that period. In fact, the glycerol part in triglyceride molecule is responsible for the high viscosity of vegetable oil, whereas the fatty acid part is 10 times less viscous than vegetable oil. During the summer of 1938, an urban bus running between Brussels and Louvain was operated on ethyl ester from palm oil. The engine performance was satisfactory and there was a report on a significant decrease in viscosity of ethyl ester as compared to that of vegetable oil. The term "biodiesel" made its first appearance in a paper published in 1988 and this term was used exponentially thereafter [6].

Biodiesel is mono alkyl esters of long chain fatty acids that can be prepared from acyl-glycerol (usually triglyceride) in vegetable oils via transesterification with short chain alcohols. The use of biodiesel is simple yet effective as it is miscible with petroleum based diesel in all proportions and can be used as fuel either in pure biodiesel or blended with petroleum based diesel fuel [10]. The blends of biodiesel and petrodiesel are often coded such as B20, which indicates the blend of 20 vol% biodiesel and 80 vol% petrodiesel. This paper will discuss details on feedstock (vegetable oils), transesterification, and biodiesel characteristics.

2. Feedstock

The feedstock for biodiesel production can be categorized as lipid feedstock and alcohol feedstock. The lipid feedstock includes vegetable oils, animal fats, and, more recently, other plant-like organisms such as micro algae and cyanobacteria. This paper focuses on vegetable oils as lipid feedstock. The vegetable oils used as lipid feedstock for biodiesel production highly depend on regional climate that is rapeseed oil in European countries and Canada, soybean oil in United States, and palm oil in tropical countries such as Indonesia and Malaysia. Coconut oil is another lipid feedstock used for synthesis of biodiesel in coastal areas. Potential non-edible oils used as lipid feedstock in India include jatropha oil (*Jatropha curcas*) and karanja oil (*Pongamia pinnata*) [11]. Table 1 summarizes oilseed price and availability which are important parameters to consider as biodiesel feedstock. Soybean oil dominates the world oilseed production while rapeseed production is second only to soybean oil. The oil content in soybean and rapeseed is 21% and 35%, respectively. Despite the lesser availability, palm oil is an interesting source for biodiesel production due to its lower price and relatively high oil content (40%). This oil also gives highest oil yield per area per year as compared to other oils.

Oilseeds contain droplets of lipid which can be extracted as vegetable oils. The major component of vegetable oils is triacylglycerol (TAG) or triglyceride (TG) which is a molecule composed of three esters of fatty acid chain (acyl group) attached to the