Renewable and Sustainable Energy Reviews 92 (2018) 235–253

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

Synthesis of biomass as heterogeneous catalyst for application in biodiesel production: State of the art and fundamental review

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ARTICLE INFO

Keywords:
Renewable energy
Biodiesel
Heterogeneous catalyst
Biomass
Reaction kinetic

ABSTRACT

Biodiesel is gaining attention as a remedy for the increasing demand of fossil fuels which is depleting rapidly. Commercial homogeneous catalysts in the biodiesel production industry are facing challenges such as separation difficulties and severe corrosion which will lead to the increment of production and maintenance cost. Herein, this paper focuses on the comprehensive review of literature reported on the usage of biomass as the precursor for the catalyst used in biodiesel production. Compared to other commercial catalysts, the usage of biomass as catalyst precursor possesses several advantages such as abundantly available, cheaper raw materials, reusable, non-toxic and biodegradable. Carbon material synthesized from biomass which acts as the efficient support for active sites due to its high porosity and surface area characteristic has been studied widely. The latest development of biomass derived basic, acidic and magnetic heterogeneous catalyst through several state of the art synthesis pathways starting from the synthesis of the supporting material (carbon) until the functionalization process to form the complete catalyst was reviewed. Apart from direct sulfonation using sulfuric acid, sulfonation by reduction and arylation were less hazardous and provided comparable active sites activity. Most biomass based catalysts exhibited good catalytic performance by providing high biodiesel yield of above 80% at optimum conditions. Besides that, various kinetic models developed from the reaction kinetic study catalyzed by biomass based catalyst were also reviewed as a preparatory stage for the scaled-up commercialization process of the studied catalyst in the biodiesel production sector. This catalyst could assist to lower the activation energy required for the reactions and thus enables higher reaction rate to reach equilibrium. Continuous research on producing high performing biomass based catalyst with minimum resources is needed in order to achieve the ultimate goal of green and sustainable biodiesel industry.

1. Introduction

Biodiesel is well known for its environmental friendly properties as a potential alternative fuel to replace the current fossil fuel derived diesel. As a renewable source of energy, biodiesel is non-toxic, biodegradable, emits far lesser pollutants and has lower sulfur and aromatic content compared to fossil fuels [1]. There are four general methods available to produce biodiesel, which are direct use and blending, micro-emulsion, thermal cracking and transesterification. Among the methods, transesterification process gains the highest attention from researchers since it usually produces biodiesel with higher combustion efficiency [2].

Generally, transesterification reaction is being carried out by reacting vegetable oil feedstock with short-chain alcohol in the presence of catalyst. Homogeneous base catalyst such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) [3] are commonly used to catalyze the transesterification of refined vegetable oil. Due to the soap formation in base catalyzed reaction when using crude vegetable oil feedstock with high free fatty acid (FFA) content, homogeneous acid catalyst such as phosphoric acid (H_3PO_4), *p*-toluenesulfonic acid (PTSA) or sulfuric acid (H_2SO_4) [4] are being introduced as pre-treatment to reduce the FFA content. Nevertheless, the usage of homogeneous catalyst has been continuously associated with challenges such as difficulty in the separation of homogeneous phase products, non-recyclable and huge cost increment on wastewater treatment system to neutralize the catalyst before discharging [5,6]. In addition, enzymatic catalyst such as lipase can also demonstrate high performance in catalyzing various vegetable oil feedstocks even with substantial FFA contents.

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https://doi.org/10.1016/j.rser.2018.04.056
Received 3 July 2017; Received in revised form 28 March 2018; Accepted 14 April 2018

However, the huge cost of enzyme still renders it a large barrier for commercialization in the biodiesel production industry. Heterogeneous catalyst which is easily separable and recyclable has shown to be a promising alternative with comparable performance to homogeneous catalyst. Heterogeneous catalyst derived from biomass has been researched extensively in recent times as it has the potential to lower the production cost. Invariably, biomass will be first converted into carbonaceous material to be used as catalyst support for the incorporation of desired functional active groups [7]. Biomass with high calcium carbonate content can also be directly transformed into calcium oxide base catalyst for transesterification process [8].

Utilization of biomass waste for the synthesis of catalyst will not only reduce the cost of catalyst raw material, but also serves as a solution for the disposal of biomass waste generated from various human and agricultural activities. Every year, more than 5 billion metric tons of biomass waste will be produced from the agricultural sector [9]. Zooming into Malaysia's agricultural sector, it was estimated that solid biomass waste will increase from 80 million tons in 2010 to 110 million tons in 2020 [10,11]. Based on a typical case study in oil seed production industry, various biomass wastes will be continuously produced starting from the harvesting stage and extraction of oil seeds until the final production of refined oil. For example, in a conventional palm oil mill and refinery plant, large amount of oil palm tree residuals will be produced such as empty fruit bunch, palm kernel shells, oil palm trunks and palm seed cakes. These biomass residuals produced from palm oil mill can be obtained at very low cost [11].

Fig. 1 shows the various sources of biomass waste produced in Malaysia in 2012 including those from timber, sugarcane, rice and palm oil industry. Oil palm waste had contributed 94% of biomass waste with the remaining 4% of wood residue from timber industry, 1% from rice mill waste and 1% of waste from sugarcane industry [10]. In the palm oil industry, oil palm fronds and trunks are collected from the plantations while empty fruit bunch (EFB), shells, kernels and palm oil mill effluents (POME) are produced from the mills [11]. They have the potential to be transformed into higher value products for different applications.

Although reviews based on the usage of biomass as feedstock for biofuels production are available, reviews on the application of biomass derived catalyst specifically for the production of biodiesel are still rare to the best knowledge of the authors. The usage of biomass as catalyst precursor for biodiesel production is able to fulfill the sustainable concept of fully utilizing all the available renewable sources in a closed cycle. Besides that, this paper also focuses on the catalyst synthesizing pathways and the reaction kinetics study which will provide great contribution to the design of large-scale commercial production plant and reduce the overall biodiesel production cost.

In view of these, the objectives of this paper are aligned to highlight the latest synthesis routes of various types of catalysts including basic, acidic and magnetic catalysts derived from different types of biomass. The performance of these catalysts in biodiesel production industry will also be compared thoroughly and to provide better insights on their roles in the current environmental friendly and sustainable framework. Besides that, another highlight of this paper is to review the fundamental study pertaining to the suitability of the selected kinetic models fitted into biodiesel production reaction for scaled-up commercial heterogeneous catalyzed biodiesel production industry in the future.

2. Biomass as precursor for carbon based catalyst

Biomass residues can be found in abundance after various human agricultural activities such as harvesting and oil extraction. In the past, biomass wastes usually have very low market value and their potential has often being overlooked. Plant biomass is mostly composed of carbon structure which can be transformed into high performing carbon materials. In recent years, numerous researchers had been utilizing low cost biomass by transforming it into high quality and value-added products through various post-handling processes.

Biomass is a reliable and sustainable source that can be converted into porous carbon material as a catalyst support. Biomass based catalysts are known to be non-toxic, biodegradable and have higher surface area than conventional catalysts such as Amberlyst-15 [12]. Shu et al. [13] was one of the pioneers who had started utilizing vegetable oil asphalt as the biomass source for producing carbon support. Since then, a lot of other researchers had turned their attention to synthesize high performing biomass based catalyst for various applications such as transesterification and esterification of vegetable oils to produce biodiesel [14] and hydrolysis of biomass into primary sugar or other value-added products such as furfural [15].

Fig. 2 illustrates an overall diagram of the carbon synthesis process through different pathways. The synthesis of carbon material can be conducted either with or without activation treatment. For activation treatment, an additional treatment step with activating agent is required at the initial carbon synthesis process. Generally, the carbon material can be synthesized through hydrothermal carbonization (HTC), template-directed synthesis and also direct thermal treatment. HTC is usually carried out in the presence of water where a mixture of water and biomass will be heated at high temperature. On the other hand, template directed method will be performed by first incorporating the template with the biomass material before carbonization. Direct carbonization is the most straight forward method whereby the biomass will be directly heated without mixing with any other compounds.

2.1. Hydrothermal carbonization

Hydrothermal carbonization (HTC) is a thermochemical treatment

Fig. 1. Various sources of biomass generated annually from different industries in Malaysia in 2012 with specific breakdown on palm oil industry [10].