Renewable and Sustainable Energy Reviews 42 (2015) 1223–1233

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

Deoxygenation of fatty acid to produce diesel-like hydrocarbons: A review of process conditions, reaction kinetics and mechanism

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ARTICLE INFO

Article history:
Received 1 June 2014
Received in revised form
3 September 2014
Accepted 28 October 2014

Keywords:
Deoxygenation
Renewable resource
Fatty acid
Diesel-like hydrocarbons
Operating conditions

ABSTRACT

Deoxygenation process of fatty acid as a renewable resource to produce diesel-like hydrocarbons is one of the alternatives to address drastic shortage of crude oil-based fuels in the near future. Catalytic deoxygenation process of fatty acid is getting attention from both academia and industry. Researchers have tried different techniques in the fatty acid deoxygenation to enhance the production of diesel-like hydrocarbons. This review paper elucidates the influence of tmain operating conditions towards achieving optimum yield and selectivity of desired products. The reaction pathways, the reaction kinetics as well as recent progress in deoxygenation of fatty acid for production of diesel-like hydrocarbons are also reviewed.

Contents

1. Introduction

Growth in road transportation sector is currently steering the demand for fuel oils. It has been predicted that the world demand for diesel fuel will grow faster than any other refined oil products toward 2035, as illustrated in Fig. 1 [1]. Diesel fuel demand is predicted to grow from 26 million barrels per day in 2012 to around 36 million barrels per day by 2035. Meanwhile, the demand for gasoline will moderately increase from about 23 million barrels per day in 2012 to 27 million barrels per day by 2035. In the same period, slight increases in demand will occur for ethane/LPG, naphtha, bitumen, lubricants waxes still gas, coke, direct use of crude oil, etc. On the other hand, demand for residual fuel will globally decrease in the coming years [1].

Due to consumption of diesel fuel derived from diminishing conventional crude oil that will continue in the next decades,

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http://dx.doi.org/10.1016/j.rser.2014.10.099
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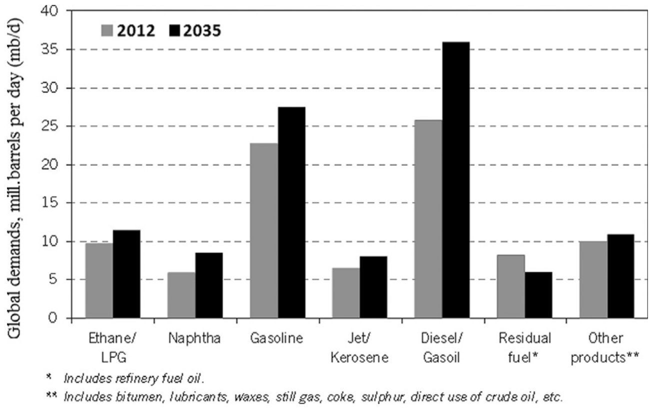

Fig. 1. Global demands for diesel fuel in 2012 and forecast in 2035 compared to other refined oil products [1].

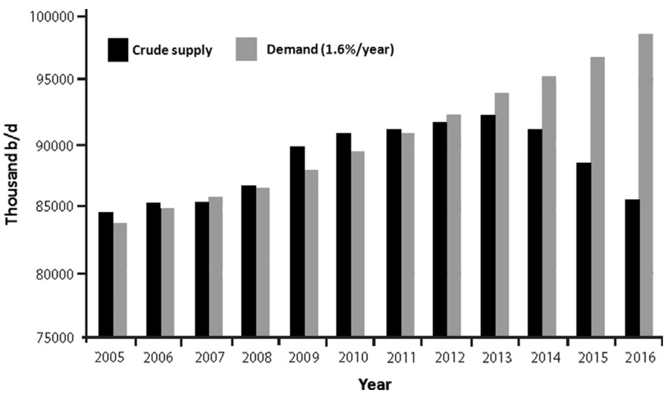

Fig. 2. Global crude oil supply and projected demand [2].

exhaustion of fossil fuels is predicted. Comparison between the most probable crude oil supply and the most likely demand requirements has been reported by the International Energy Agency (IEA) [2], as can be seen in Fig. 2. Conventional crude oil supply exceeded the demand from 2009 to 2011. However, in 2012 and 2013, the demand consistently exceeded supply. Then, from 2014 onwards, the conventional crude oil supply will be shortfall. Meanwhile, the demand will constantly increase due to rapid growth in human population.

Therefore, extensive studies on biofuels productions from various renewable feed stocks and related technologies have been carried out for many years [3–8]. Among others, fatty acids are renewable resources that can be produced in mass scale and used as feedstock for deoxygenation reactions to synthesize diesel-like hydrocarbons [9–14]. Diesel-like hydrocarbons contain *n*-alkanes and alkenes that are hydrocarbons similar to those found in diesel fuel obtained by refining crude oil in petroleum refineries [15]. Thus, this option provides interesting alternative to support future energy demand.

Fatty acids are found in plant oils/fats and animal oils/fats [16–21]. Besides of fatty acids, plant oils/fats and animal oils/fats contain triglycerides with the main constituent. Fatty acids are formed during enzymatic hydrolysis of triglyceride especially when the oils are kept in humid atmosphere [22–27]. Fatty acid can also be formed during purification of vegetable oils and fats [28–30]. It can be produced at a sufficiently high rate in many countries. For example, in the United States, tall oil fatty acid can be obtained by vacuum distillation of crude tall oil which is side stream from pulp and paper industry [31]. Tall oil fatty acid mainly consists of palmitic acid, oleic acid and linoleic acid. The total production of tall oil in the United States was 845,000 t in 2004 [32]. Meanwhile, Malaysia and Indonesia, as the world's top-two

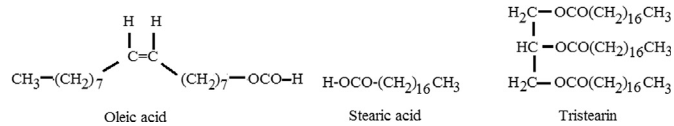

Fig. 3. Molecular structures of stearic acid, oleic acid and tristearin.

largest crude palm oil (CPO) producers, produce palm fatty acid distillate (PFAD) which is the by-product of physical refining process of CPO [33]. Malaysian refineries produced PFAD with the total amount of 750,000 t in 2008 [34]. PFAD contains more than 90% palmitic acid and is comparatively far cheaper than CPO. It is generally sold as a source of industrial fatty acids for non-food applications such as laundry soap industries [35–38]. It can also be used to produce renewable energy sources through suitable thermochemical means.

Fatty acids are carboxylic acids with long aliphatic chains, which are either saturated or unsaturated [39]. Saturated fatty acids are fatty acid that have no carbon–carbon double bond such as palmitic acid, stearic acid and lauric acid. Unsaturated fatty acids are fatty acids with one or more carbon–carbon double bonds for example: oleic acid, myristoleic acid and linoleic acid. Meanwhile, triglycerides are esters derived from glycerol and tree fatty acids. They are named according the fatty acid components, for example, tristearin contains three molecules of stearic acid. Other examples of triglyceride are trilaurin, tripalmitin and triolein. Molecular structures of stearic acid, oleic acid and tristearin can be seen in Fig. 3.

There are several alternative techniques recently developed to produce diesel like-hydrocarbon using fatty acid such as catalytic cracking, hydrotreating and catalytic deoxygenation. Catalytic cracking technology is used to break down high-molecular-mass into fragments of lower molecular mass [40–45]. Hydrotreating process involves the removal of oxygen though the introduction of hydrogen into the fatty acid or triglyceride molecules either using metal catalyst or oxide catalysts to produce *n*-alkanes [46–50]. Meanwhile, deoxygenation involves removal of the carboxyl group in the fatty acid as carbon and/or carbon monoxide using a supported metal catalyst, thereby producing alkane and alkene as diesel-like hydrocarbons [51]. Very encouraging results have been reported recently [46–48].

During the past few year, researchers reported mechanism and kinetic model of fatty acid deoxygenation over supported metal catalyst to produce diesel-like hydrocarbons. It also reported that operating parameters were important to optimize selectivity/yield of diesel like-hydrocarbon in the deoxygenation process. The operating parameters include supported metal catalyst type, feed type, temperature, reaction atmosphere, feed rate (residence time), catalyst amount and the presence of solvent. This review summarizes reaction pathways and kinetic models of deoxygenation fatty acid. Subsequently, the roles of the operating conditions that are employed for optimum yield and selectivity of diesel-like hydrocarbon are highlighted. This paper also highlights recent progress in deoxygenation of fatty acid to produce diesel-like hydrocarbons. In addition, highlights on future directions for this option are also provided.

2. Reaction pathways and kinetic models of deoxygenation of fatty acid to produce diesel-like hydrocarbons

Lestari et al. [51] proposed general saturated fatty acid deoxygenation reaction steps under inert atmosphere over supported metal catalyst that involve several reaction pathways, as can be seen in Fig. 4. Under inert atmosphere, the presence of hydrogen during the process is achieved via dehydrogenation of unsaturated