Review

Recent developments and key barriers to advanced biofuels: A short review

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A B S T R A C T

Biofuels are regarded as one of the most viable options for reduction of CO_2 emissions in the transport sector. However, conventional plant-based biofuels (e.g., biodiesel, bioethanol)'s share of total transportation-fuel consumption in 2016 was very low, about 4%, due to several major limitations including shortage of raw materials, low CO_2 mitigation effect, blending wall, and poor cost competitiveness. Advanced biofuels such as drop-in, microalgal, and electro biofuels, especially from inedible biomass, are considered to be a promising solution to the problem of how to cope with the growing biofuel demand. In this paper, recent developments in oxy-free hydrocarbon conversion via catalytic deoxygenation reactions, the selection of and lipid-content enhancement of oleaginous microalgae, electrochemical biofuel conversion, and the diversification of valuable products from biomass and intermediates are reviewed. The challenges and prospects for future development of eco-friendly and economically advanced biofuel production processes also are outlined herein.

1. Introduction

As climate change becomes an issue of ever-stronger concern in the world, ever-various efforts are being devoted to its resolution. Recently, the International Energy Agency (IEA) proposed the 2 °C scenario (2DS) to cope with this issue. The 2DS has been widely quoted by many policy makers and researchers. According to this scenario, carbon dioxide (CO_2) emissions in 2060 should be reduced by 70% relative to the 2014 level. To achieve this target, CO_2 reductions in the transport sector is important, since transportation accounts for about 23% of total CO_2 emissions. Recently, electricity has been regarded as a promising option for CO_2 reduction in transportation (Yabe et al., 2012). However, transport biofuel is predicted to be the key alternative energy for CO_2 mitigation in the transport sector (Ahlgren et al., 2017). According to mobility model results for the 2DS released by the IEA, biofuels' share of total transportation-fuel consumption by 2060 is predicted to be 30.7%, followed by electricity at 27%. In order to meet this future demand, biofuels production must be increased by a factor of 10. Unfortunately, several major barriers to the realization of biofuels' implementation target still exist.

The first barrier is the shortage of feedstocks. In 2016, the share of biofuels in the transport sector was about 4%, corresponding to an 8×10^7 TOE (tone of oil equivalent). While the average annual growth rate of biofuels for 2006–2016 was 14.1%, the rate for the past two years is only 1.5%. This lower recent growth rate is due to the limited feedstock supply. Currently, over 90% of total biofuels (e.g., bioethanol, biodiesel) are made from edible biomass such as grain or vegetable oil. So, conventional biofuels made from edible feedstocks might not be the right candidates for meeting the increasing demand for transport biofuels in the future (Ho et al., 2014). Advanced biofuels produced from various different inedible feedstocks are promising alternative options (Fig. 1). Active work has been done to convert lignocellulosic biomass to various biofuels (Brown, 2015; Jiang et al. (2017a,b); Lynd et al., 2017). As one result, cellulosic ethanol is at an early stage of commercialization (Chen et al, 2016). Other cellulosic biofuels produced by thermochemical technologies are also close to commercialization. And there are feedstocks other than lignocellulosic biomass that might be used for biofuel production as well.

The second barrier to the realization of biofuels' implementation target is the blending wall of conventional biofuels. Blending biofuels with petro-fuels is known to impact various fuel properties (Bwapwa et al., 2017; Dechambre et al., 2017). Since conventional biofuels such as bioethanol and biodiesel, unlike petro-fuels, contain oxygen in their molecules, they have different fuel properties. As such, biofuels are not fully compatible with existing petroleum infrastructures. The oxygenated functional groups in biofuels have several adverse effects. They can react with refinery and pipeline metallurgy as well as with biofuel components to form gum acids and other impurities that lead to poor
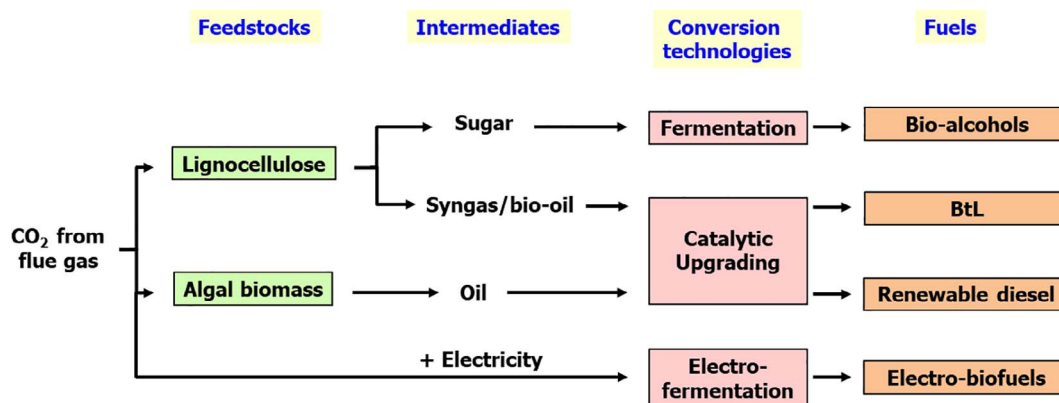

Fig. 1. Advanced biofuels from various inedible feedstocks.

storage stability (Bridgewater, 2012). The oxygen molecule also increases the affinity of biofuel to water and reduces, thereby, the energy density of biofuels. The energy contents of bioethanol and biodiesel are only 65 and 89% of petro-fuels, gasoline and diesel. Therefore, bioethanol and biodiesel (e.g. fatty acid methyl ester, FAME) are allowed to mix with petro-fuels only at low percentages, up to 10% for ethanol and 7% for biodiesel.

Finally, although advanced biofuels have many advantages (as mentioned above), their costs are much higher than those of petro-fuels or even conventional biofuels (Barros et al., 2015; Rastogi et al., 2018). The poor fuel economy of advanced biofuels is the most important barrier to their commercialization. Unless this and the other major barriers noted above are overcome, advanced biofuels might not be implemented. So, work has been underway to resolve those challenging issues.

Although many review articles on the topic of advanced biofuels are available elsewhere (Alfenore and Molina-Jouve, 2016; Cheon et al., 2016; Jiang et al. (2017a,b); Ullah et al., 2018), most are limited to the utilization of cellulosic biomass-derived resources. We focus herein on drop-in, microalgal and electro biofuels, which recently have been highlighted in both the academic and industrial sectors. The main objective of this paper was to introduce these advanced biofuel technologies and the key barriers to their commercialization. The paper thus provides an updated overview of the recent technical developments and progress with regard to the relevant advances and selected challenging issues. Furthermore, the outlook for feasible options including drop-in biofuel conversion of algal oil, electro-bioconversion of C1 gases, and the biorefinery processes for multiple biofuels and biochemical productions and their practical applications is presented.

2. Recent developments and key barriers to advanced biofuels

2.1. Drop-in biofuels

As mentioned above, the oxygen content in a biofuel leads to different properties from those of petroleum-based fuel, which properties significantly limit biofuels' fuel-blending rates. Therefore, oxygen-free biofuels are required to improve both fuel quality and blending rates. The key reaction in the production of a high-quality biofuel is the deoxygenation reaction, including hydrodeoxygenation (HDO), decarboxylation and decarbonylation. The HDO reaction is a well-established reaction in which the oxygen in molecules is removed as H_2O in the presence of H_2 and a catalyst. However, HDO requires a large amount of H_2 (generally 300–420 $m^3 H_2/m^3$ vegetable oil), which is the main issue in the production of biofuel (Kubička, 2008). Recently, a single-step process including HDO and hydro-upgrading has been investigated for reduction of H_2 consumption in the production of high-quality biofuels (Zhang et al., 2017). Oxygen can be removed as CO and CO_2 via decarbonylation and decarboxylation, which produce

hydrocarbons with one fewer carbon than the parent compounds. These three reactions take place simultaneously in practice, and one reaction can be dominant depending on the catalysts and reaction conditions. Meanwhile, hydrogen donors have been utilized to facilitate decarboxylation and decrease the initial deactivation rate of the catalyst by acting as an *in situ* hydrogen supply. The produced oxy-free hydrocarbons, compared with first-generation fuels such as biodiesel, are highly compatible with current engines. As the price of biofuel is heavily dependent on the availability and cost of H_2, it is worth discussing how the deoxygenation reaction requires less hydrogen.

2.1.1. Hydrodeoxygenation (HDO)

Renewable biofuel has been produced from vegetable oil and animal fats using commercial processes involving HDO reactors such as UOP's Ecofining process and NEXBTL's Renewable Diesel process. Despite this, various catalysts have been investigated for HDO (Ju et al., 2016; Liu et al., 2014; Zhou and Lawal, 2016). For bi-functional catalysts, nickel and precious metals have been used as active metals, and accordingly various zeolites and mesoporous materials are used as their supports. Nickel has shown high potential for HDO reaction in terms of cost and activity, and zeolites have many merits such as the ability to control the carbon number and type (i.e., normal or isomer) of oxy-free hydrocarbons, because their acid types and numbers of acid sites are easier to adjust. Because the HDO reaction is so well understood, non-edible plant oil and microalgal oil, additionally to model compounds such as fatty acids, also have been utilized for the screening of HDO catalysts (Yang et al., 2016).

More recently, most studies have focused on single-step reactions including hydro-upgrading of oxy-free hydrocarbons as well as HDO, particularly for the production of bio-jet fuel, as summarized in Table 1. This single-step process involving bi-functional catalysts is one method to reduce the amount of H_2 consumed during biofuel production. Zhang et al. (2017) reported the hydro-conversion of waste cooking oil into biofuel over hierarchical USY-supported NiMo catalysts at 380 °C and 30 bar of H_2 in a reactor. A NiMo catalyst supported on dealuminated USY (AHFS-Y) gave the highest liquid yield, 82%, as well as the highest hydrocarbon fraction in the liquid, 70%, because dealumination of a zeolite can prevent excessive cracking of hydrocarbons. Furthermore, after mild dealumination of USY, the ratio of *iso-* to normal-paraffins in jet-range hydrocarbons can be increased by controlling the ratio of weak-acidity acid sites to strong-acidity acid sites. Ni-supported mesoporous Zeolite-Y has given a liquid yield of 68.9% in hydro-treatment of waste cooking oil at 390 °C and 30 bar of H_2 in a batch reactor (Liu et al., 2014). The highest yield of jet-range hydrocarbons in the liquid product, 66.4%, was obtained, and the selectivity for aromatic hydrocarbons was approximately 20%. Additional upgrading of the produced hydrocarbons was required. Herskowitz et al. (2013) demonstrated a single-step continuous process for the production of *iso*-diesel from soybean oil using a Pt/SAPO-11-Al_2O_3 pellet catalyst in a bench-scale