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Thermochemical conversion of triglycerides for production of drop-in liquid fuels

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ABSTRACT

The increasing demand for transportation fuels, coupled with the depletion of petroleum resources and growing environmental concerns necessitates the development of efficient conversion technologies for the production of biofuels. Thermochemical approaches hold great promise for converting biomass into liquid fuels in one step using heat and catalysis. Several thermochemical processes are employed in the production of liquid biofuels depending on the target product properties: 1) direct thermal conversion; 2) catalytic cracking; 3) hydrodeoxygenation of plant oils and animal fats. Since enormous quantities of liquid fuels are consumed by transport vehicles, converting biomass into drop-in liquid fuels may reduce the dependence of the fuel market on petroleum-based fuel products. In this review, we summarize recent progress in technologies for large-scale direct thermochemical production of drop-in biofuels. We focus on the technical aspects critical to commercialization of the technologies for production of drop-in fuels from triglycerides, including cracking catalysts, catalytic cracking mechanisms, catalytic reactors, and biofuel properties. We also discuss future prospects for direct thermochemical conversion in biorefineries for the production of high grade biofuels.

Contents

1. Introduction

In 2011 the world annual primary energy consumption was estimated at 13,113 million tonnes of oil equivalent (Mtoe) [1]. Fossil fuels accounted for 81.6% of consumption, with oil (31.5%), coal (28.8%) and natural gas (21.3%) as the major fuels [1]. Energy consumption worldwide has never been higher than now as a result of population growth and social development [1,2].

The transportation sector is one of the major energy consumers and accounts for about one fifth of total energy consumption worldwide [3]. As the world's population grows and means of transportation become more readily available, the need for fuels,

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especially liquid fuels, will become greater in the future [4]. However, progressive depletion of petroleum-based fuels has led to a global energy crisis [5]. The decreasing availability of petroleum resources also coincides with an increasing emission of greenhouse gases that are responsible for global warming. There is therefore a great need for methods that can decrease greenhouse gas emissions, and this has led to an increasing interest in biofuels.

Substantial research has been carried out to find alternative fuels that can replace gasoline and diesel. The optimal solution would be an alternative that is equivalent to the conventional fuels, i.e. compatible with existing infrastructure, but also one that is sustainable and will decrease CO_2 emissions, reducing the environmental anthropogenic footprint [6].

Renewable biomass sources can be converted to environmentally friendly fuels and are a logical choice to produce fuel oil [7,8]. Fuel oil derived from biomass is clean since it has negligible sulfur, nitrogen and ash content, producing lower emissions of SO_2, NO_x and soot than conventional fossil fuels. Zero net emission of CO_2 can be achieved because the CO_2 released from biomass can be recycled photosynthetically by plants.

The United States and other countries have set up domestic programs/strategies to derive more energy from renewable feedstocks in order to decrease their dependence on foreign petroleum. In February 2010, the US Environmental Protection Agency (EPA) finalized regulations under the Energy Independence and Security Act of 2007 that made significant changes to the renewable fuel standard in the Energy Policy Act of 2005. The changes aim to boost domestic biofuel production by increasing the minimum volume of renewable fuel that transportation fuel sold in the United States must contain.

The targets set by the European Union (EU) renewable roadmap indicate that every EU member state should substitute 20% of its fuels with biofuels by 2020 [9]. China also set up a road map for the development of renewable energy by the National Development and Reform Commission in 2007. The road map also requires that 20% of total liquid fuels are to come from renewable sources by 2020 [10].

Although biofuels have shown steady growth in recent years, they still only represent 3% of global transport fuel consumption [11]. About 97% of all transportation energy in the United States is currently derived from non-renewable petroleum and consumes 63% of all oil used there. Foreign oil accounts for more than half of all oil used in the United States [12].

Currently, a variety of liquid biofuels are under development, such as biodiesel in the EU and bio-ethanol in China. Total EU (EU27) biodiesel production for 2010 was over 9.5 million metric tonnes, an increase of 5.5% from 2009 [13]. Production of bioethanol in China was 645.9 million gallons in 2011 [14].

There are numerous triglycerides available for biofuel production. World production of plant oil rose to 175 million tonnes in 2014, with palm oil accounting for 1/3 of total oil output [15]. However, production of “first generation” biofuel from crude plant oil is limited because the majority is used for human food.

Waste triglycerides, such as waste cooking oil, waste fish oil and acid oil from soap stock are important renewable feedstocks for drop-in fuel production [3–5,16,17]. These feedstocks have no competition from human consumption or agriculture, and their use can also solve environmental issues associated with disposal of waste organic materials.

In recent years, utilization of waste triglycerides for liquid fuel production has attracted much attention. Taking plant oil as an example, approximately 20% of the waste oil can be recovered after consumption, amounting to 36.8 million tonnes. On the other hand, only about 5% of acid oil (waste triglycerides) can be recovered from soap stock in plant oil refining plants, which is approximately 8.8 million tonnes according to the total amount of plant oil processed worldwide.

Thermochemical conversion is the major method for production of liquid biofuels from biomass. As the term implies, thermochemical conversion involves the use of heat to change biomass to other forms. At the same time, catalysts/chemical reactants are used to transform basic molecular structures into ones that are more useable as fuels. Thermochemical processes have several advantages compared with biological processes, including greater feedstock flexibility, conversion of both carbohydrate and lignin into products, faster reaction rates, and ease of transportation.

This review will provide an overview of the present status of direct thermochemical processes for the production of liquid biofuels from triglycerides. The variety of raw materials, operating conditions, choice of catalyst, and reaction mechanisms will be discussed. Changes in the molecular structures during the thermochemical processes will be considered as an important indicator of the quality of the biofuels. These considerations will be used to give a synopsis of the thermochemical processes of different feedstocks. The properties of the products derived from biomass are compared with petroleum-based fuels as the benchmark. Finally, production of drop-in bio-fuels through thermochemical processes on an industrial scale is discussed.

2. Thermochemical conversion of triglycerides

2.1. Processing properties of triglycerides

Triglycerides, the main constituents of animal fats and vegetable oils, are composed of a glycerol molecule attached to three fatty acid molecules. The carbon chain length and number of double bonds in a fatty acid vary depending on the source of the oils. Triglycerides are easier to convert into liquid transportation fuels than cellulosic biomass because they are already high-energy liquids that contain less oxygen.

The main properties of triglycerides from plant oil and animal fats are listed in Table 1. According to reports, triglycerides can

Table 1
Basic properties of example plant oils and animal fats.

Physicochemical properties	Lard [18]	Sunflower oil [19]	Soybean oil [20]	Palm oil [20]	Waste oil [20]
Density (kg/m^3)	940	908	920	928	919
Heat value (MJ/kg)	39.6	39.7	–	–	–
Viscosity (mm^2/s)	36.4[a]	34.6[a]	7.5[b]	8.2[b]	9.3[b]
Elemental analysis					
C%	–	77.35	77.2	76.7	76.9
H%	–	11.54	11.1	11.5	11.3
O%	–	11.11	11.7	11.8	11.8
Fatty acid composition (%)					
C14:0	1.4	–	0.07	0.99	0.22
C15:0	0.1	–	–	–	–
C16:0	24.1	5.1	10.47	43.03	9.28
C16:1	2.4	–	0.1	0.19	0.49
C17:0	0.4	–	0.08	0.1	0.07
C18:0	14.0	2.8	3.34	4.31	3.95
C18:1	39.4	26.4	24.96	39.47	54.55
C18:2	14.2	65.7	53.28	10.82	29.67
C18:3	0.8	–	6.46	0.29	0.25
Boiling range (°C)					
Initial boiling point	–	–	545.7	345.2	382.9
25% distill-off temperature	–	–	608.0	594.5	618.4
50% distill-off temperature	–	–	611.8	602.0	623.4
75% distill-off temperature	–	–	615.4	607.5	628.2
Final temperature	–	–	636.0	626.1	774.1

[a] Measured at 40 °C.
[b] Measured at 100 °C.