Synthesis of Diesel Blending Stocks from Vegetable Oils

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Introduction

The high cost of transportation fuels, larger environmental footprints of fossil fuels and limited petroleum reserves in the world have re-kindled the need to invest in research on renewable resources. Bio-diesel and renewable diesel have the potential to become a viable alternative to diesel fraction derived from petroleum-based feedstock as a cleaner burning fuel in the future.

Vegetable oils are mainly made up of triacylglycerides (TAG). Fatty Acid Methyl Ester (FAME) is the technology identified with bio-diesel. It involves reacting vegetable oils with methanol in the presence of a catalyst to make methyl esters of the fatty acids in TAG. This methyl ester mixture, containing 11% oxygen, is directly blended in diesel. Hydroprocessing of a vegetable oil involves removing oxygen from TAG. It involves hydrogenolysis of the TAG moiety, resulting in the formation of water and saturation of the internal double bonds of the fatty acids. The combined process is called hydro-deoxygenation (HDO). The diesel obtained this way is called the hydrogenated renewable diesel (HRD)

Currently, several variations of HDO technology are being developed. Neste Oil's NExBTL process uses heterogeneous catalysts of Pt and Pd supported on carbon to minimize the use of hydrogen by removing oxygen mainly in the form of CO and CO_2 [1]. The CANMET Energy Technology Centre of Natural Resources Canada's SuperCetane process is based on a conventional hydrotreatment of catalyst [2]. Petrobras, the Brazilian Oil Company's H-Bio diesel process involves the catalytic hydrotreatment of vegetable oil and conventional refinery mineral oils [3].

This study focuses on evaluating the advantages and disadvantages of bio-diesel versus hydrogenated renewable diesel from a processing perspective.

Materials and Methods

The experiments are conducted in agitated pressure vessels under elevated temperature and pressure using vegetable oil. The catalysts are either made internally at DuPont or obtained from several different catalyst companies and then modified.

In a typical experiment, the bio-oil/catalyst mixture is placed in the reactor and the mixture is heated to the reaction temperature under desired hydrogen pressure. After the reaction is over, the reaction mass is brought back to ambient conditions and the product is discharged into sample bottles. The product is analyzed by gas chromatography (GC), mass spectrometry (MS), and Thin Layer Chromatorgraphy (TLC).

Results and Discussion

Based on the experimental results, it can be surmised that the efficacy of promoted and unpromoted bimetallic base metal catalysts on solid acid supports is quite high for HDO reactions. However, the hydrogen uptake for bio-reforming process is much higher than that for refinery hydrotreatment processes. The FAME process, on the other hand does not involve hydrogen treatment of the vegetable oil feed. The methyl esters obtained are directly blended in without any additional processing.

Future work involves increasing the competitive advantage of the HDO process for upgrading vegetable oils into diesel blending stocks. This will require maximizing the carbon efficiency of the process by designing the catalyst system in such a way that it minimizes the CO and CO_2 formation. Furthermore, it is expected that the use of vegetable oils from DuPont's genetically adjusted seeds will help reduce the hydrogen consumption and lower the pressure and temperature of the process.

Significance

Bio-diesel has the potential to be a cleaner burning fuel of the future and a sustainable product based on renewable resources.

References

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