Oxygen-assisted partial hydrogenation of biodiesel fuel over an alumina-supported palladium catalyst to produce hydrotreated fatty acid methyl esters

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Abstract: The partial hydrogenation of jatropha–oil–derived biodiesel fuel (BDF) with a high degree of unsaturated fatty acid estails was successfully performed on an alumina-supported palladium catalyst under mild conditions (100ºC and 0.5 MPa) to produce hydrotreated fatty acid methyl esters (H-FAME) enriched in monounsaturated components. The co-feeding of proper amounts of molecular oxygen (400–1500 ppm) resulted in enhanced activity and durability of Pd catalyst. The produced H-FAME exhibited significantly improved oxidation stability and uncompromised cold-flow properties, and they can serve as an excellent source of high-quality BDFs, particularly for high-blend fuels.

Keywords: Biodiesel, Partial hydrogenation, H-FAME.

1. Introduction

Conventional biodiesel fuel, mainly containing fatty acid methyl esters (FAME) is a sustainable diesel fuel produced primarily by transesterification of many kinds of oils. Many countries, especially ASEAN plan to gradually increase the BDF/fossil-derived diesel blending ratio from the current value. However, biodiesel-blended diesel has poor oxidation stability, causing many technical problems, such as damage to the injector, engine, and emission systems. Hence, in order to improve the oxidation stability of biodiesel without compromising cold-flow properties, partial hydrogenation of polyunsaturated FAMEs to monounsaturated FAMEs is required. In addition, while biodiesel must meet certain standards, the process of hydrogenation may also yield low concentrations of impurities, such as sulphur (S)- and nitrogen (N)-containing compounds, which have not yet been regulated by international biodiesel standards[1]. These impurities, which varying in concentration depending on the production area, may cause deactivation of the metal catalyst responsible for partial hydrogenation[2, 3]. Therefore, enhancement of the durability, activity, and selectivity of the catalyst is essential. In this study, we focused on the improvement of catalyst stability for the partial hydrogenation of polyunsaturated FAMEs to monounsaturated FAMEs produced by Jatropha oil-derived FAME with the proper amounts of molecular oxygen in a fixed bed reactor.

2. Experimental (or Theoretical)

$Pd/\gamma\text{-}Al_2O_3$ catalyst was prepared by impregnation with an aqueous solution of $Pd(NH_3)4Cl_2{\cdot}xH_2O$, keeping the Pd loading at 0.5 wt.%. As a result, a $Pd/\gamma\text{-}Al_2O_3$ catalyst with a surface area of 203 $m^2\ g^{-1}$ and a Pd metal dispersion of 42.3% was obtained. Partial hydrogenation of Jatropha oil–derived BDF over $Pd/\gamma\text{-}Al_2O_3$ catalyst was carried out in an up-flow fixed-bed reactor under mild conditions (100 ºC and 0.5 MPa of H_2). In some cases, a small amount of oxygen gas was co-fed with the oil feedstock and hydrogen flow in order to make clear the effect of oxygen to the activity and durability of Pd catalyst.

3. Results and discussion

The effect of oxygen content in biodiesel on the activity and stability of the Pd/Al_2O_3 catalyst under reaction conditions of T=100ºC, P=0.5 MPa, WHSV=144 h^{-1} is demonstrated in **Fig. 1**. The oxygen gas was added with hydrogen before biodiesel arrive at catalyst bed. The results clearly indicate that the additions of small amount of oxygen into biodiesel are dramatically effective for not only catalyst activity but also stability of Pd/Al_2O_3 catalyst. At lower oxygen content (< 811 ppm), the catalyst activity and stability on the linear increase with increasing oxygen content. The addition of 811 ppm oxygen was most effective for catalyst stability in this reaction condition. At higher oxygen content (>1853 ppm), the catalyst stability decreases with increasing oxygen content. This was due to the Pd metal was gradually oxidized to PdO under higher oxygen content. But the catalyst activity increase with increasing oxygen content at higher oxygen content though this detail mechanism is not still clear.

Table 1 presents the FAME composition and some fuel properties of FAME, hydrogenated FAME (H-FAME) without oxygen, and H-FAME with 811 ppm oxygen at the same polyunsaturated FAME conversion (around 90%). After reaction, a decrease in polyunsaturated FAME along with an increase in monounsaturated FAME and saturated FAME were detected. And also, acid value and water content decrease after partial hydrogenation. In addition, partial hydrogenation can improve the oxidation stability of FAME from 0.8 to 14.1 h (H-FAME), which meet the fuel standard regarding oxidation stability (e.g. > 10 h, EN14214). And also, the oxidation stability of H-FAME with 811 ppm oxygen shows good results (13.2 h) although decrease of the oxidation stability was concerned by the addition of oxygen because there is a possibility that increase of oxygen promote to react with the olefinic fatty acid chains[4].

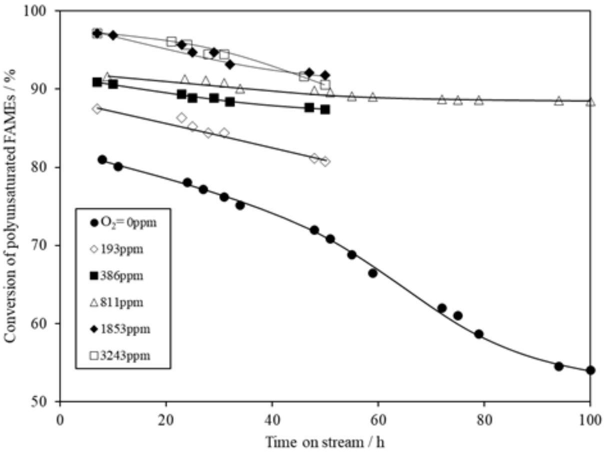

Fig. 1 Effect of oxygen addition on the activity and stability of the Pd/Al_2O_3 catalysts for partial hydrogenation of Jatropha FAME.
Reaction conditions: P=0.5MPa, T=100°C, $WHSV$=144 h^{-1}

Table 1 The FAME compositions and fuel properties of biodiesels before and after partial hydrogenation reaction

	FAME	H-FAME	H-FAME with 811ppm oxygen
Conversion of polyunsaturated FAMEs (%)	–	90.9	89.0
FAME composition (%)			
Saturated FAME	21.6	33.1	31.2
Mono-unsaturated FAME	44.1	62.9	64.5
Di-unsaturated FAME	33.3	3.0	3.5
Tri-unsaturated FAME	0.2	0	0
Acid value (mg-KOH/g)	0.23	0.18	0.14
Water content (ppm)	337	263	270
Pour point (°C)	13	18	18
Oxidation stability (h)	0.8	14.1	13.2

4. Conclusions

In summary, oxygen-assisted partial hydrogenation of Jatropha oil–derived BDF to H-FAMEs has been successfully realized using a $Pd/\gamma\text{-}Al_2O_3$ catalyst under mild reaction conditions. The activity and durability of the above catalyst in H-FAME synthesis was significantly improved by co-feeding of molecular oxygen with Jatropha oil–derived BDF contaminated with small amounts of heteroatom-containing species under an atmosphere of pressurized hydrogen. Most importantly, this upgrading process can be used to synthesize H-FAME with high oxidation stability and uncompromised fuel properties to be used as a potential BDF source, particularly for high-blend fuels.

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