Thermal Stability of Biodiesel Fuel as Prepared by Supercritical Methanol Process

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For pursuit of sustainable energy, biodiesel fuel (fatty acid methyl esters) has been given much attention as a substitute for fossil diesel fuel. Currently, biodiesel is commonly produced by alkali-catalyzed method. In this method, however, waste oils/fats rich in free fatty acids and water are difficult to be utilized efficiently since the former results in producing undesirable saponified products and the later hinders complete conversion of oils/fats. A non-catalytic supercritical methanol method is an attractive process to overcome such problems. However, this process requires rather high temperature and high pressure conditions.

In such sever conditions, thermal stability of biodiesel fuel is important. Especially, it is well known that unsaturated fatty acids are rather reactive and thus vulnerable to denaturations such as oxidation and geometric isomerization from *cis-* to *trans-*configuration. This geometric isomerization may have adverse effects on some fuel characteristics such as cloud point, cold filter plugging point (CFPP), pour point, kinetic viscosity and so on. For instance, *trans-*isomer is known to have higher melting point than that of *cis-*configuration. It is thus important to know the relation between these denaturations on fuel properties. In this study, therefore, thermal stability of fatty acid methyl esters in supercritical methanol was studied.

As main components of biodiesel, three kinds of fatty acid methyl esters (methyl oleate (C18:1), linoleate (C18:2) and linolenate (C18:3) purchased from Aldrich-Sigma) were, respectively, exposed in supercritical methanol at temperatures between 270℃ and 380℃ for a designated reaction time. After the exposure, obtained reactants were subjected to high performance liquid chromatography (HPLC), fourier transform infrared spectrometry (FT-IR) analyses. As actual biodiesel samples, on the other hand, biodiesel from linseed oil, safflower oil, rapeseed oil and palm oil were subjected to a similar exposure and analyses mentioned above. Furthermore, cold flow properties were evaluated by a mini pour/cloud point tester.

As a result, it was found that the poly-unsaturated fatty acid methyl esters such as methyl linoleate and methyl linolenate were partly degraded and isomerized into *trans-*type one with a rise in temperature, especially above 300℃. Moreover, these changes were more likely to take place for fatty acids with higher degree of unsaturation. The effect of thermal degradation and isomerization on cold flow properties is, however, not noteworthy as exposed to supercritical methanol. From these lines of evidence, it was clarified that biodiesel is not deteriorated in terms of cold flow properties by the supercritical methanol treatment.