Near infrared spectroscopy can detect proper condition of biodiesel fuel production

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Introduction

In order to reduce CO_2 emission, biodiesel fuel (BDF) is one of the possible alternatives from fossil fuel, as it is "carbon neutral energy". BDF is methyl esters of fatty acids made by transesterification reaction of vegetable oils, animal fats or waste oils. In using BDF, it is important to adjust injection settings for reducing NOx and PM emissions, Because BDF has variety of fuel properties caused by compositional ratio of methyl esters in it.

At moment, however, production cost of present catalyst method is still high, and it is the reason that the use of BDF does not expand rapidly. So, we are attempting to develop new method; continuous supercritical method. In this method, reaction is done in supercritical state of methanol. And it needs, different from the catalyst method, just simple separation procedures, neither neutralization nor purification.[1] But, on the other hand, supercritical state may cause decomposition of fatty acids in case of higher temperature and longer reaction time.[2] These decomposed products are thought as short chain free acids or it's methyl esters, and have also influence on fuel properties. So, it is important to monitor the products of reaction for proper BDF production.

In this study, we tried to discriminate the products with decomposed fatty acids from that without decomposed fatty acids by SIMCA method.

Materials and methods

Sample preparation

Sixty eight samples were used, most of which were produced by supercritical fluid reactor, "SCW-R14" (OM-Labotech, Japan). The materials were virgin canola oil on the market (Nisshin, Japan) and methanol (purity >99.5%). The ratio of oil and methanol was 1:42 in molar ratio. The reaction conditions were set to 150, 250, 300, 350, 400 and 450°C in temperature; 5, 10, 20, 30 and 40 MPa in pressure; and 2, 3, 4, 6, 8, 10 min in time, respectively. In setting the above mentioned, methanol was supercritical state in the condition of 250°C or more in temperature and 10 MPa or more in pressure. The products divided into two portions after supercritical process. The lower portion is glycerol and oil which did not react and the upper one is BDF and methanol. The upper portion after leaving at a night sitting was used for measurement.

NIR measurements

Instruments used were Bran+Luebbe Infra Alyzer 500 with transflectance cell for liquid samples which has 0.5 mm path length.

Spectra were collected at 2 nm intervals, from 1100 nm to 2500 nm. Spectra data were analysed by chemometrics software package, "The Unscrambler" (Camo AS, Norway).

Chemical analysis

The material oil was transesterificated with catalyst (NaOH) to determine composition of fatty acids by GC-MS, "GC-MATE II" (JEOL, Japan). As a result, the main composition of fatty acid in this oil was palmitic acid (C16:0), stearic ccid (C18:0), oleic acid (C18:1), and lenoleic acid (C18:2). lenolenic acid (C18:3) was observed, but its concentration was very little. So, in this study, we defined 'BDF' as 'the compound of four kinds of fatty acid methyl esters (methyl palmitate, methyl stearate, methyl oleate, and methyl lenoleate)'. Qualitative and the quantitative analysis of these fatty acid methyl esters in production were done by GC-MS.

Results and discussion

Figure 1 shows raw spectra of all samples. These spectra have a strong band at 2276 nm and, also, some peaks were observed, though they were not too strong, at 1576, 1702, 2070 nm. These characteristics were quite similar to those of methanol.

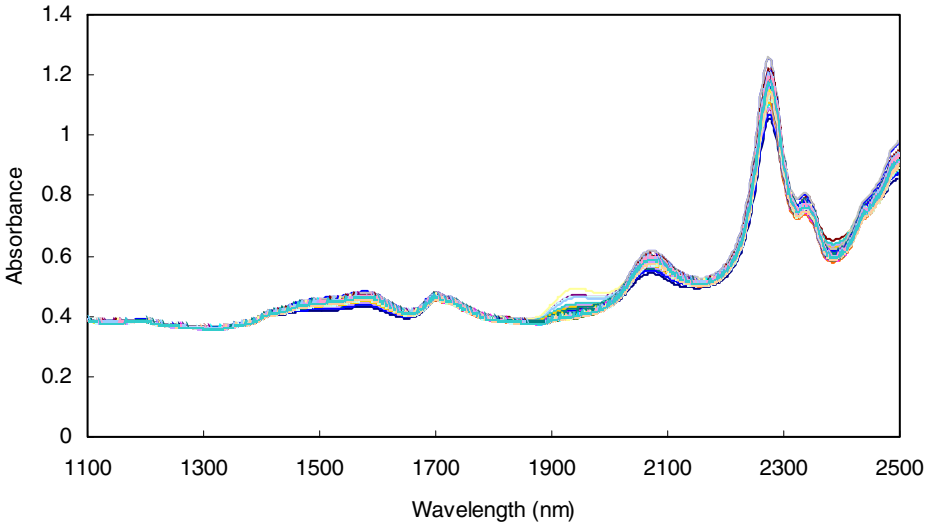

Figure 1. Raw spectra of all samples.

As a result of chemical analysis, the range of BDF productions was 0 to 14.8 mg mL^{-1}MeOH, and 50% or more of BDF was Methyl Oleate. And BDF production was not observed without supercritical state, in other words, in the state which 250°C or less in temperature and 5 MPa in pressure.

First, all samples were submitted to PCA. Figure 2 shows scores biplots of PC1 versus PC2. In this plot, two groups were observed. One is tended to be proportional, and the other is scattered in the second quadrant. The clear tendency could not be observed to the later group.

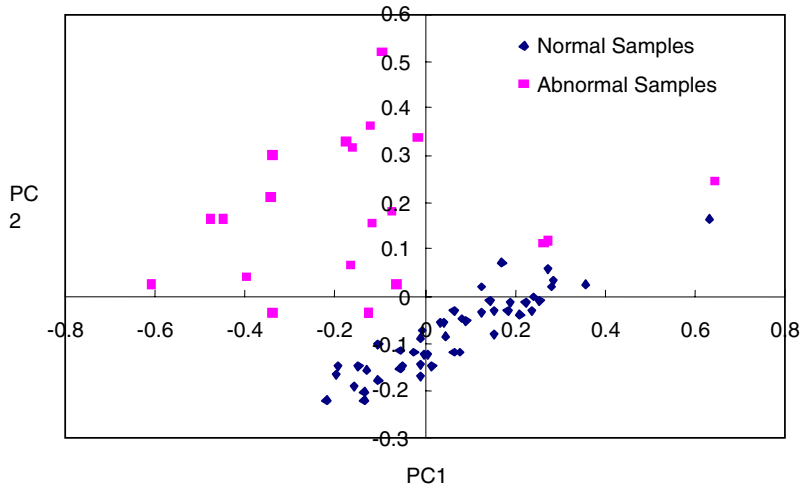

Figure 2. PC1 versus PC2 score plot.

Figure 3 shows chromatgram of various samples by GC-MS. Most of the samples had only peaks of BDF [Figure 3(a)]. But, in some samples, the peaks of unknown materials were observed [Figure 3(b)]. These were considered as middle or short chain fatty acid methyl esters, and never included in normal BDF. The samples with various stuffs were treated in higher temperature or longer reaction time. So, these were considered as decomposed stuff of triglycerides in supercritical treatment. In this study, the samples without decomposed stuffs were defined as normal BDF group, and the other was defined as abnormal BDF group.

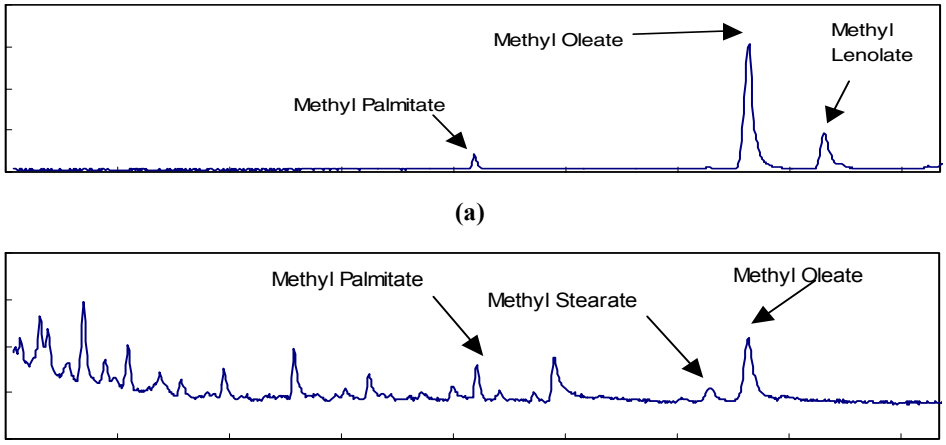

Figure 3. Gas Chromatgram of productions. (a) 350°C-40MPa-8min treatment. (b) 400°C-40MPa-8min treatment.

The loading of PC1 had a large peak in 2276 nm in Figure 4. This peak is a combination of mainly C–H stretch and C–H deformation, which is related to CH_3. In the loading of PC2, there are reverse peaks with PC1 and those wavelengths were 2380 nm and 2070 nm, which is related in structure of ROH.[3]

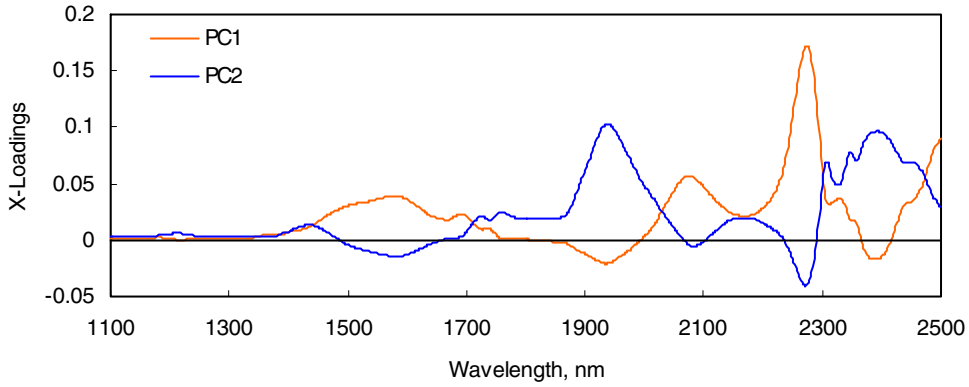

Figure 4. x-loadings of PC1 and PC2.

From the above, average spectra of each groups were calculated. It was shown that the large difference between two groups. The difference wavelengths were same as peak of x-loadings in Figure 4. These peaks are related in methanol (CH_3OH). Then, the spectra of methanol were compared with these average spectra, and it was similar to that of normal sample group. Therefore, the structure of methanol was changed in abnormal sample group. It was considered that methanol was also decomposed because of thermal cracking.[4]

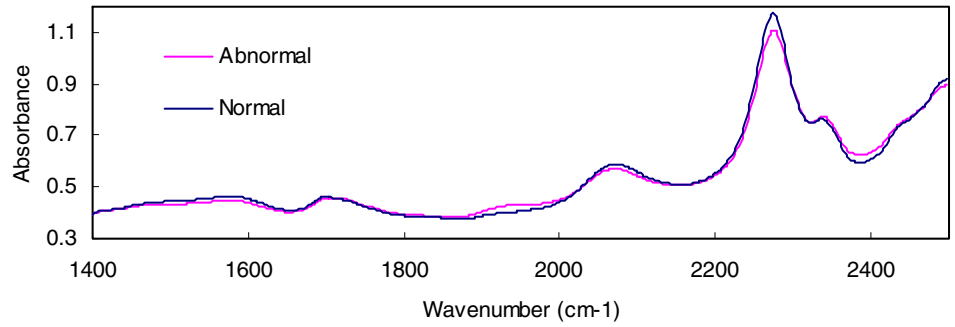

Figure 5. Average spectra of both samples.

Finally, we tried to discrimination of abnormal samples from normal samples.

A principal component model from normal BDF group was developed. The SIMCA method was applied to the spectra of normal and abnormal samples using previous model. Then, abnormal

samples were correctly discriminated from normal group. The abnormal samples were scattered, these seem to be classified into some groups.

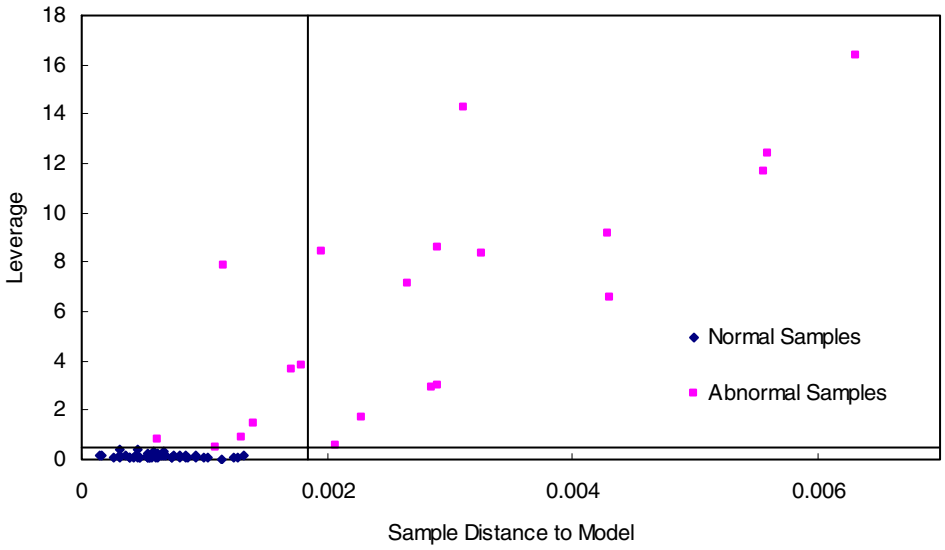

Figure 6. Discrimination of abnormal BDF products by SIMCA.

Conclusion

The NIRS method was found that samples with decomposed products were discriminated, from normal samples containing just methyl esters, by the SIMCA method.

Acknowlegements

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