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Prediction of Chemical Properties of Biodiesel Fuels from the Properties of Raw Materials with Neural Network Analysis

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The chemical properties of BDFs were predicted by neural network analysis with the properties of the raw edible oils as the input learning characteristics. The model used in the analysis had a multi layer perception structure. 22 kinds of typical edible oils on the market were converted to BDFs using the transesterification of methanol with alkali catalyst method. To build the model of causal relation between raw materials and products, the measured properties of nine raw oils and BDFs were used as learning data. To verify the model, the properties of the other 13 BDFs were predicted from the properties of the raw oils. The kinematic viscosity, density, and cloud point of the BDFs were predicted well using suitable combinations of input characteristics of the raw oils. The accuracy of the predicted values depended on the combinations of the selected characteristics. However, the acid value of BDFs was poorly predicted.
Key words: neural network, biodiesel fuel, edible oil, prediction, alkali catalyst method

1. INTRODUCTION

With the signing of the Kyoto Protocol in 1997, the output of greenhouse effect gas from developed nations is being restricted.[1] Methods for reducing greenhouse gas emission, especially carbon dioxide exhausted from combustion engines, are being investigated in many laboratories. A biodiesel fuels (BDFs), which are made of raw plant oils, are one solution and are favorable for a carbon neutral philosophy. Especially, the cultivation of a fatty plant such as rape seed has been promoted as supplying a raw material for BDFs in Europe where the use of the diesel engine is widespread.[2]

To ensure the quality of a BDF, the processing conditions of the BDF production must be adjusted properly. If the quality of the raw oil is quickly known, the adjustment becomes easy. Furthermore, if the quality of the produced BDF is predicted from the combination of the quality of the raw oil and the processing conditions, the composition of the exhaust gas can be estimated without a combustion test. To build the above prediction system, the causal relation between the characteristics of raw oils and the properties of produced BDFs was computed with neural network analysis in this study. Furthermore, for the neural network model obtained, the potential of the prediction of the chemical properties of a BDF from the chemical properties of the raw oil is demonstrated.

Neural network analysis is a method of mimicking the prediction and judgment of the human brain, which has the ability to learn from various experiences. This method does not need numerical formulas that would be indispensable in other computer simulations. The neural network model is built by only the causal relation between the cause and the result. After the model is built by many leaning events, the prediction of an unknown result becomes possible by input new causes. As successful examples, the identification of paints and plastics from the FT-IR spectrum and the source of olive oil in Italy from the fatty acid composition have been reported.[3,4]

2. EXPERIMENT

2.1 Production of BDF

22 kinds of edible oils on the market were converted to BDF by the alkali catalyst method as follows. The edible oil and methanol were mixed to 1:24 by mole ratio in a flask, and sodium hydroxide was added to the mixture as 1.0 wt% of the edible oil. The mixture was heated at 60 °C for 60 minutes.[5] After the reaction ended, the flask was cooled and left, and the BDF-layer was separated from the methanol-layer including a soap. The BDF-layer was washed once with NaCl saturated solution including 0.5 V/V% of acetic acid and twice with NaCl saturated solution. To remove water, an excess amount of sulfuric anhydride magnesium was added. The BDF was thus obtained.

2.2 Chemical analysis

Chemical properties were measured for the raw edible oil:

1) density [g/cm^3] measured with a pycnometer
2) kinematic viscosity [cm^2/s] measured with a capillary viscometer (JIS K2283)
3) acid value [mg-KOH/g-oil] measured by titration with KOH in ethanol and diethyl ether mixture (JIS K3331)
4) moisture content [μg-H_2O/g-oil] measured by the Karl Fischer method
5) fatty acid composition measured by Gas chromatography (GC) after conversion to the corresponding methyl ester (JIS K3331)
6) mean molecular weight calculated from the fatty acid composition
7) Fourier transform-infrared (FT-IR) spectrum
8) elution pattern in HPLC detected with an ultraviolet adsorption (UV) or refractive index (RI) detector

Table I Experimental values of the chemical properties of raw edible oils.

Oil type	Density [g/cm^3]	Kinematic viscosity [cm^2/s]	Acid value [mg/g]	TPM value [%]	Moisture content [μg/g]	Fatty acid composition					Molecular weight [g/mol]
						C16	C18	C18:1	C18:2	C18:3	
Rape seed oil	0.9048	0.1989	0.0835	12.0	64.98	0.049	0.022	0.659	0.186	0.084	879.6
Safflower oil	0.9004	0.2169	0.0532	6.5	63.27	0.046	0.021	0.824	0.109	0.000	881.3
Corn oil	0.9064	0.1872	0.1951	15.0	69.07	0.112	0.021	0.274	0.585	0.007	872.3
Sesame oil	0.9077	0.2004	1.3333	14.0	38.85	0.097	0.055	0.386	0.462	0.000	875.4
Olive oil	0.8994	0.2210	0.7820	7.7	ND	0.102	0.022	0.812	0.058	0.005	876.3
Grape seed oil	0.9089	0.1872	0.4388	ND	91.69	0.065	0.040	0.184	0.711	0.000	876.3
Rice oil	0.9054	0.2187	0.1509	14.0	35.96	0.179	0.021	0.461	0.330	0.010	870.4
Sunflower oil	0.8995	0.2271	0.0603	5.0	60.00	0.041	0.034	0.878	0.047	0.000	882.2
Soybean oil	0.9104	0.1835	0.0956	14.5	59.63	0.143	0.055	0.200	0.516	0.087	871.3
Blended oil	0.9060	0.1917	0.1192	14.0	59.70	0.090	0.032	0.452	0.371	0.055	875.7
Rape seed oil	0.9051	0.2034	1.4138	50.5	166.93	0.043	0.020	0.669	0.191	0.078	881.0
Waste rape seed oil	0.9089	0.2360	7.2628	30.5	73.37	0.070	0.026	0.660	0.178	0.065	877.4
Sesame oil	0.9070	0.1984	ND	13.1	67.94	0.093	0.052	0.397	0.459	0.000	876.6
Rice oil	0.9055	0.2176	0.1981	15.0	70.15	0.184	0.021	0.425	0.359	0.011	868.9
Rice oil	0.9084	0.2387	1.6801	21.5	75.53	0.199	0.024	0.435	0.341	0.000	867.1
Safflower oil	0.8994	0.2182	0.0409	8.5	59.79	0.055	0.023	0.792	0.130	0.000	880.5
Olive oil	0.9017	0.2209	0.3326	8.2	ND	0.105	0.032	0.785	0.078	0.000	877.0
Sesame oil	0.9081	0.1984	0.0386	9.3	31.28	0.090	0.053	0.410	0.448	0.000	876.9
Corn oil	0.9083	0.1856	0.1801	14.0	64.64	0.108	0.021	0.288	0.583	0.000	873.6
Sunflower oil	0.9082	0.1914	0.1165	19.5	72.59	0.060	0.032	0.358	0.550	0.000	877.6
Soybean oil	0.9093	0.1814	0.0788	16.0	61.70	0.143	0.045	0.228	0.528	0.056	870.7
Grape seed oil	0.9100	0.1767	0.0999	19.5	44.54	0.088	0.052	0.179	0.680	0.000	873.9

ND, not determined.

Table II Experimental values of the chemical properties of BDFs.

Oil type of raw material	Density [g/cm^3]	Kinematic viscosity [cm^2/s]	Acid value [mg/g]	TPM value [%]	Cloud point [°C]	Moisture content [μg/g]
Rape seed oil	0.8655	0.0440	1.0042	22.5	-2	102.70
Safflower oil	0.8613	0.0449	1.3015	18.5	-3	58.44
Corn oil	0.8667	0.0417	0.7949	25.0	-3	78.75
Sesame oil	0.8672	0.0434	1.0559	25.5	1.5	98.51
Olive oil	0.8597	0.0451	0.6226	18.5	-1	71.71
Grape seed oil	0.8687	0.0416	1.0241	ND	ND	95.10
Rice oil	0.8657	0.0467	1.3564	2.5	2	133.10
Sunflower oil	0.8603	0.0466	1.0502	15.0	3.5	67.74
Soybean oil	0.8701	0.0437	1.1687	27.0	1	68.12
Blended oil	0.8666	0.0428	1.5852	31.5	-2	82.20
Rape seed oil	0.8662	0.0425	0.8742	ND	ND	125.65
Waste rape seed oil	0.8667	0.0462	1.1061	33.5	-4	ND
Sesame oil	0.8668	0.0435	1.6995	23.5	1	77.70
Rice oil	0.8658	0.0467	0.9275	21.5	2	74.72
Rice oil	0.8683	ND	1.9049	ND	2.5	59.02
Safflower oil	0.8620	0.0449	0.6383	21.0	-4	79.54
Olive oil	0.8599	0.0449	0.4609	19.0	-1	72.75
Sesame oil	0.8661	0.0437	0.8182	20.0	1.5	53.89
Corn oil	0.8665	0.0416	1.1431	25.5	-3.5	110.56
Sunflower oil	0.8662	0.0423	1.1922	27.5	6	80.06
Soybean oil	0.8682	0.0413	2.1090	26.5	0	67.87
Grape seed oil	0.8678	0.0405	1.1171	27.5	1.5	73.40

ND, not determined.

9) total polar materials (TPM) measured with a cooking oil tester (Testo265 developed by Testo AG)

Chemical properties were measured for the produced BDF:

1) density [g/cm^3]
2) kinematic viscosity [cm^2/s] (JIS K2283)
3) cloud point [°C] (JIS K2283)
4) acid value [mg-KOH/g-oil] (JIS K3331)
5) moisture content [μg-H_2O/g-oil]
6) TPM value

Table III Neural network prediction of the kinematic viscosity of BDFs in several combinations of learning characteristics of the raw edible oils.

Combination No.	Characteristics of raw edible oils: Oil type	Density	Kinematic viscosity	Acid value	Moisture contents	Fatty acid composition	Molecular weight	FT-IR	HPLC / UV	HPLC / RI	TPM value	Mean error [cm^2/s]
19	–	–	–	–	–	–	–	–	–	+	–	0.0005
50	–	–	–	–	+	–	–	–	–	+	–	0.0006
34	–	–	–	–	–	+	–	–	–	+	–	0.0006
25	–	–	–	–	–	–	+	+	–	–	–	0.0006
45	–	–	–	+	–	–	–	–	–	+	–	0.0006
:												:
42	–	–	–	+	+	–	–	–	–	–	–	0.0027
59	–	+	–	–	–	+	–	+	–	–	–	0.0029

+, Properties used for prediction.

2.3 Prediction with neural network analysis

For the neural network analysis to predict the chemical properties of a BDF from the properties of a raw edible oil, NeuralWorks Predict Version 3.21 (NeuralWare Co. Ltd.) was used. The measured properties of the raw edible oils were the learning input data for the neural network analysis, and the one of the properties of the BDF was the target output value. 9 of the 22 records were used for leaning the causal relation between input and target data. The other 13 records were used for verification of the correlation between measured and predicted values. The values predicted by the neural network model were evaluated using the mean discrepancies from the experimental values. The learning frequency, the number of hidden layers, and other conditions used the default values prepared in NeuralWorks Predict.

3. RESULTS AND DISCUSSION

3.1 Prediction of the kinematic viscosity of BDFs from the characteristics of raw edible oil

The chemical properties of raw edible oils are shown in Table I. The chemical properties were varied, especially the fatty acid composition. It is considered various BDFs can be produced by using raw edible oils with different characteristics. Table II shows the characteristics of the produced BDFs. The viscosity, density, cloud point, and acid value are important factors when BDFs are used as fuels. The kinematic viscosity and density influence the performance of the fuel injection pump that supplies fuel to a diesel engine. The cloud point relates to the solidifying point of BDFs in cold conditions. The acid value relates to corrosion of a fuel system.

The kinematic viscosities of BDFs were predicted from various combinations of the chemical properties of the raw edible oils. The prediction was computed with neural network analysis using the learning information of the upper group in Table I and the experimental data of the kinematic viscosity in Table II as the target value. The results for various combinations of the input characteristics are shown in Table III. In the case of kinematic viscosity, the values for BDFs could be predicted from only the HPLC/RI chromatogram of the raw materials within 0.0005 cm^2/s (shown as No. 19). That is to say, we can predict the physical property of a product from the chemical character of the raw material. It is considerable that the viscosity of a BDF depends on the molecular length of the fatty acid residue, and the characteristic of molecular length appears in the HPLC elution pattern of the raw material. Therefore, it is thought that the viscosities of BDFs can be predicted from the HPLC patterns of the raw materials.

With other combinations of the input characteristics used, the kinematic viscosity could also be predicted, e.g., by the combination of the molecular weight and FT-IR spectrum. On the whole, good predictions were observed in the HPLC/RI pattern used for the combinations. This is because this characteristic is directly influenced by the molecular length of raw oils. For example, as shown in Fig. 1, the elution patterns of HPLC/RI were different for the different oil types. For the characteristics of the elution pattern, we input the position and intensity of the peaks as the leaning data. Although each elution peak could be identified with investigation of the fatty acid content, the identification is needless in the neural network analysis because the analysis only recognizes pattern differences and does not determine which factors are responsible for a signal.

3.2 Prediction of other properties of BDFs

Table IV shows the results for the prediction of the kinematic viscosity, density, cloud point, and acid value

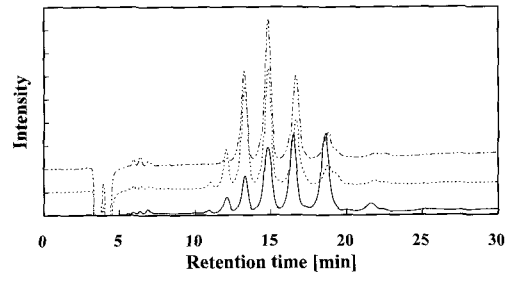

Fig. 1 Example of a HPLC/RI chromatogram. ——, rape seed oil; – – –, soybean oil; — - - —, corn oil.

Table IV Neural network prediction of properties of BDFs

Properties of BDFs	Combination No.	Chemical properties of edible oils: Oil type	Density	Kinematic viscosity	Acid value	Moisture contents	Fatty acid composition	Molecular weight	FT-IR	HPLC / UV	HPLC / RI	TPM value	Mean error
Kinematic viscosity	19	–	–	–	–	–	–	–	–	–	+	–	0.0005 [cm^2/s]
Density	52	–	–	–	–	–	–	+	–	+	–	–	0.0008 [g/cm^3]
Cloud point	63	+	–	–	–	–	+	–	–	–	–	–	1.1 [°C]
Acid value	84	–	+	–	–	–	–	–	–	–	–	+	0.3524 [mg/g]

+: Properties used for prediction.

of BDFs; the tabulated combinations are the predictions giving the smallest error in each target property. For all target properties, the qualities of prediction depended on the combinations of the selected input characteristics as for the case of kinematic viscosity.

In the prediction of the density of a BDF, the combination of the molecular weight and the HPLC pattern determined with the UV detector of raw oil was useful as the learning characteristic. It is thought this characteristic implies the content of unsaturated fatty acid residues, and the residues influence the density owing to their space filling effect. For the cloud point, the combination of the oil type and fatty acid composition was a good characteristic for the prediction. The goodness of this combination suggested that the cloud point was determined by the kind of raw oil, for example, the molecular length and degree of unsaturation of the fatty acid residue. The acid value was predicted using a combination of the density and TPM value of the raw oil. However, the prediction has a large error. The acid value is affected by the reaction conditions in production, but it is surprising that it can be predicted.

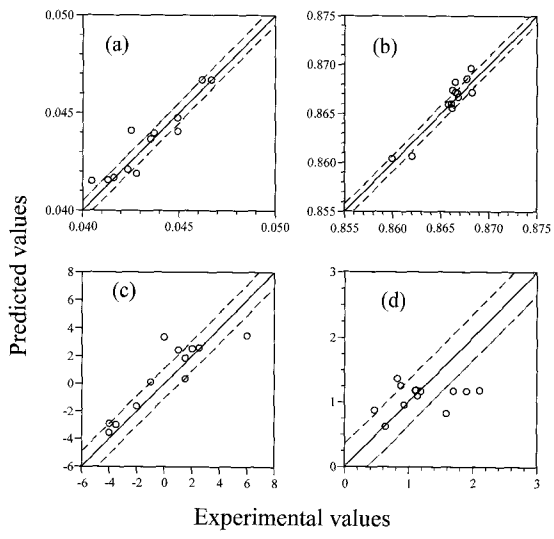

Fig. 2 Relationship between the experimental values of properties of BDFs and the values predicted from the properties of raw edible oils with neural network analysis. (a) Kinematic viscosity in cm^2/s for No. 19, (b) density in g/cm^3 for No. 52, (c) cloud point in °C for No. 63, and (d) acid value in mg-KOH/g-oil for No. 84. Solid lines indicate the equivalence of experimental and predicted values. Broken lines indicate the mean discrepency from the equivalent.

The relationships between experimental and predicted values of the kinematic viscosity, density, cloud point, and acid value are shown in Fig. 2. Examples giving the smallest mean error for each target (Nos. 19, 52, 63 and 84, respectively) are shown. The mean discrepancies from Table IV are also shown, and the plots of kinematic viscosity, density and cloud point are sited well for each equivalent line. However, the acid values are not well sited because of the low accuracy of their prediction as described above. It seems that the introduction of new characteristics of raw oil is necessary to obtain a better prediction of the acid value.

4. Conclusions

The chemical properties of BDFs produced from the raw edible oils could be predicted with neural network analysis. Good predictions were made for the kinematic viscosity, density, and cloud point of BDFs. The prediction accuracy depended on the selected combination of raw material characteristics. However, the prediction of the acid value was poor and it is suggested that new characteristics are needed for good prediction.

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