

THERMOANALYTICAL ASSESSMENT OF THE QUALITY OF EDIBLE AND TECHNICAL OILS

M. Wesolowski

ANALYTICAL CHEMISTRY DEPARTMENT, FACULTY OF PHARMACY,
A. K. MARKSA 107, PL 80-416 GDAŃSK, POLAND

An investigation of the thermal decomposition of fish oils and motor lubricating oils resulted in the elaboration of a new method, which, by utilizing the relationship between the temperatures of mass losses and the changes in the chemical composition due to the oxidative and hydrolytic decomposition of fish oils and to the processes occurring in lubricating oils in the course of their service in the oils system of combustion engines, allows estimations of the physicochemical properties of these oils.

It is known from common practice that the quality assessment of edible and technical oils on the basis of their physicochemical properties requires considerable labour. In this respect an investigation was undertaken to utilize the changes taking place in the course of the determination of oil products, which should be reflected by the thermal decomposition curves of the samples examined, for the quality assessment of fish oils and for determination of the usability of lubricating oils for further service.

Experimental

Materials tested

Medicinal cod-liver oils were used, which had been collected in 1972-82. Some of the samples originated from pharmacies in Gdańsk and Gdynia and from the Galenic Laboratory of the "Cefarm" Pharmaceutical Provision Enterprise in Gdańsk. The remaining samples were obtained from the Fish Processing Works in Gdynia. The refined fish oils, both edible and technical, collected in 1976-82, were also received from the Fish Processing Works in Gdynia. The samples of refined fish-meal residual oils were obtained from the Fish-Meal Plant of the "Dalmor" Company for Overseas Fishing and Fishing Service in Gdynia.

The M-20 Bp, MS-20 p, Marinol CB SAE-30 and DS-11 motor lubricating oils, both new and used, the latter being sampled directly from the oil system of marine

engines after a few to a few thousand hours of service, were received from the Laboratory for Engine Fuels and Lubricants in Gdynia.

Testing technique

The densities, the refractive indices, and the saponification, iodine and acid numbers of the fish oils were determined according to the procedures given in the literature [1]. The water contents, kinetic viscosities, flash points and the contents of foreign solids and of oxide ash of the lubricating oils were determined according to appropriate standards [4, 5].

The DTA, TG and DTG thermal decomposition curves were recorded with an OD-103 derivatograph model 3427. All measurements were made under identical conditions. The weighed 200 mg samples in a platinum crucible 9.5 mm in diameter were heated under the atmosphere of the furnace at a heating rate of 5 deg min^{-1} up to a final temperature of 873 K. $\alpha\text{-Al}_2\text{O}_3$ was used as reference. Each curve was recorded at least three times.

The temperatures of the beginning and end of the thermal decompositions of the oils were read off the TG and DTG curves, whereas the temperatures of 1, 5, 15, 30, 50 and 75% mass losses were read only off the TG curves.

Results and discussion

The chemical compounds formed in the course of the rancidification of fish oils change the shapes of the thermal decomposition curves of the oils [1, 3]. It has been found that along with the deterioration of an oil's quality, the beginning of the deflection of the TG curve from the base-line is shifted towards lower temperature values and, in addition, the curve is characterized by a less steep course. The same dependence is observed for the temperatures associated with the successive mass losses. Further investigation has indicated the existence of relationships between the temperature of the beginning of mass loss and the values of density, reflective index, and the saponification, iodine and acid numbers over the entire range of the values. The linear correlation factors for medicinal cod-liver oils [1], edible fish oils [2], technical fish oils and fish-meal residual oils [3] exhibit higher values than the critical ones at a probability level of 0.01.

On the basis of the results obtained, it has been found that the estimation of the degree of deterioration of fish oil should be carried out from the temperatures associated with the initial segment of the mass loss in the TG curve. If the equations for the regression lines are used, the temperature ranges can be determined which should correspond to the beginning of the decomposition and the 1, 5 and 15%

mass losses; so that it may be established whether the product under examination meets the requirements of the standard. When adequate equations are applied, the values of density, refractive index, and the saponification, iodine and acid numbers for the oil in question can also be estimated.

The changes in the chemical composition of a lubricating oil, caused by the presence of its oxidation products and by the incomplete combustion of the fuel, are reflected by both the evaporation process and the thermal decomposition of the product examined [4–6]. This is particularly distinctly illustrated by the temperature range of about 100 degrees between the beginning of mass loss and the beginning of the nearly linear segment of mass loss. Analysis of the temperature values for this range, together with the values of kinetic viscosity, flash point and the contents of foreign solids and oxide ash, has shown that the less used the oil, the more the temperature range is shifted towards lower values.

The values of the correlation factors for the temperatures of the beginning, the end and the successive mass losses vs. viscosity and flash point indicate the existence of a linear relationship between the variables. The correlations between the temperatures of the successive mass losses and the content of ash oxide are questionable value, whereas for the foreign solids the correlation factors assume lower values than the critical ones at a probability level of 0.01.

As in the case of fish oils, linear equations were used to determine the temperature ranges to which the temperatures of the initial stage of thermal decomposition of M–20 Bp, MS–20 p [4], Marinol CB SAE–30 [5] and DS–11 [6] oils should correspond, so that it might be estimated whether the viscosity and the flash point of the sample examined met the requirements of the appropriate standard. The regression line equations for the temperatures of the beginning and the 5% mass loss were also established, and on this basis physicochemical properties of the lubricating oil could be evaluated after determining these temperatures from the thermal decomposition curve.

Conclusions

The investigation of fish oils and lubricating oils has proved the usefulness of thermal analysis methods for estimating the degree of rancidification of medicinal cod-liver oils, edible and technical fish oils and fish-meal residual oils, as well for estimating the further service performance of M–20 Bp, MS–20 p, Marinol CB SAE–30 and DS–11 lubricating oils.

The changes which occur in the chemical compositions of fish oils in the course of their oxidative and hydrolytic decomposition, as well as in lubricating oils, are well reflected by their DTA, TG and DTG thermal decomposition curves. For the

quantitative estimation of an oil's quality, only the TG and DTG curves can be used. The statistical assessment of the measurements made has shown that, in contrast to the results obtained with the DTA method, the TG (DTG) measurements are characterized by high precision. The values of the coefficient of variation indicate that the former can be counted among the less accurate scientific measurements.

References

- 1 M. Wesołowski, *Sci. Pharm. (Wien)*, 54 (1986) 11.
- 2 M. Wesołowski, *Fette, Seifen, Anstrichm.*, in press.
- 3 M. Wesołowski, *Seifen, Öle, Fette, Wachse*, 112 (1986) 231.
- 4 M. Wesołowski, *Thermochim. Acta*, 91 (1985) 265.
- 5 M. Wesołowski, *Thermochim. Acta*, 99 (1986) 333.
- 6 M. Wesołowski, *Thermochim. Acta*, 101 (1986) 9.

Zusammenfassung — In Zusammenhang mit der Ausarbeitung einer neuen Methode, die die Abschätzung der physikalisch-chemischen Eigenschaften von Fischölen und Motorschmierölen ermöglicht, wurde eine Untersuchung über die thermische Zersetzung dieser Öle durchgeführt. Als Grundlage dafür diente der Zusammenhang zwischen der Masseverlusttemperatur und der mit der oxidativen bzw. hydrolytischen Zersetzung von Fischölen und den Alterungsprozessen von Motorschmierölen in Verbrennungsmotoren in Verbindung stehenden Veränderung der chemischen Zusammensetzung.

Резюме — Исследование термического разложения рыбьего жира и моторных смазочных масел привело к разработке нового метода, который позволил определить физико-химические свойства жиров и масел, используя связь между температурами потери веса и изменением их химического состава, обусловленного окислением и гидролитическим расщеплением рыбьего жира, а также процессами, происходящими со смазочными маслами при использовании их в масляной системе двигателей сгорания.