RHEOLOGICAL PROPERTIES OF FRUIT DISTILLATES

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Abstract

The article is focused on the experimental detection of rheological characteristics of fruit distillates. Distillates were processed with spirit of alcohol volume of 52%. 5 samples were researched. We observed dependency of dynamic viscosity, kinematic viscosity, density, and fluidity on temperature. The results were graphicly processed and regression equations, and the coefficient of determination were made. The stated courses declare strong exponential dependence of observed rheological characteristics on temperature. As different types of fruit distillates contain different additives, these may have influence on researched rheological characteristics. A specific part is devoted to thermogravimetric analysis – measures the mass (change of the mass), provides information on the content of components. Interpretation of the obtained TGA curves provides information about processes running in the materials, changes of physical and chemical properties and conditions of it, e.g., phase transitions, drying, oxidation stability, thermal stability, chemical reaction, denaturation, compositional analysis, purity, etc. Thermal analysis are respectable methods for analysis foods samples and alcohol.

Key words: *rheological properties, viscosity, thermogravimetric analysis, distillate.*

INTRODUCTION

While measuring alcohol of 99%, the density of a sample at a given temperature is same. On the other hand, as far as fruit distillates are concerned, we have alcohol volume 52 % and the left over 48 % are demineralized water and additives which are different for each sort. We can find out different courses depending on type of distillates by measuring rheological properties – density and viscosity.

Viscosity is defined by inner friction in liquid, it is the rate of resistance against mutual movement of molecules of fluid and it is the result of interaction between molecules (*Krempaský, 1982*). Viscosity can be kinematic and dynamic. Dynamic viscosity of fluids is functionally dependent on temperature and pressure, which means it decreases with increasing temperature and it increases with increasing pressure. Kinematic viscosity is determined by ratio of dynamic viscosity to density at a given temperature. Dynamic and kinematic viscosity of oils decrease considerably with increasing temperature. It is caused by aggregation of molecules at lower temperatures and by breaking up clusters at increasing temperature and by extending free volume in fluid, which means the difference between total volume of fluid and actual volume of present molecules (*Štěpina & Veselý, 1985*). Density is a quantity dependent on temperature and pressure. Density means the weight of defined volume of substance at a given temperature and pressure, usually 20 °C and 0,1 MPa. Density is an important figure for conversion units of volume and weight, and it is also important for calculating kinematic viscosity from dynamic one (*Štepina & Veselý, 1985*).

Thermogravimetric Analysis (TGA) are regarded as being the main techniques applied to improving the functional properties and process conditions. Can be investigated process of evaporation, destruction individual components and another. Effects where we can observed by TGA are compositional analysis, chemical reaction, desorption (drying, evaporation), enthalpy change, identification, oxidative stability and thermal stability. The result of the differential thermal analysis is a DTA-curve, which graphically shows the dependence of the temperature difference between the studied and reference sample (in units of electrical voltage, normally mV, since this difference is sensed as a voltage difference on the thermocouples under the studied and reference sample) on the temperature. On the DTA curve, we observe areas of zero values, when no action is taking place, and peaks. Peaks of positive values are caused by exothermic events and are called exoeffects, while peaks reaching negative values, so-called endoeffects, are caused by endothermic events (*Hrubá, 2018*). The term “differential” indicates that the difference in behaviour between the material under study and a supposedly inert reference material is examined. In this manner the temperature at which any event either absorbs or releases heat can be found. This allows the determination of, e.g., phase transition temperatures and the study of order-disorder transitions and chemical reactions. Similarly, heat capacity measurements can be performed, although DTA and DSC differ significantly in the ease and precision of such measurements. These two methods are ideally suited for quality control, stability, and safety studies. These thermal analysis methods can be conducted simultaneously with other measurement methods to provide a greatly enhanced ability to understand material behaviour (*Lexa, 2002*). In cases blends contains starch, ethylene alcohol and water interpretation of the TGA results becomes quite difficult and usually important errors are committed in the determination of blend composition (*Vega, 1996*; *Tripodi, 2022*). Curves DTA and DTG we can help to identify exact temperature to process. The aim of the study was to detect experimentally rheological characteristics of fruit distillates. We researched five different samples with the same alcohol volume focusing on dependency of dynamic viscosity, kinematic viscosity, density, and fluidity on temperature. The second part of the research was focused on the interpretation of the obtained TGA curves.

MATERIALS AND METHODS

The measurement was carried out on five samples of distillates – cherry, plum, pear, peach, and apricot. The alcohol volume of all examined samples was 52 % at temperature 20 °C. The measurement of density was carried out on densimeter Mettler Toledo DM40. The principle of measurement of density is based on electromagnetic induced oscillation of U-shaped glass tube. Dynamic viscosity was measured on viscometer DV2T fy Brookfield. The principle of measurement is based on measurement of torque of spindle rotating in the sample at constant speed. Dynamic viscosity derived from Newton's law is characterized by a relationship:

$$\tau = \eta \, grad \, v \qquad (1)$$

where: $grad\, v = \frac{dv}{dh}$ - the size of velocity gradient (s^{-1}),
τ - shear stress (Pa),
η - dynamic viscosity (Pa.s).

The basic unit of dynamic viscosity is Pa.s., but a thousand times smaller unit mPa.s is usually used (*Krempaský, 1982*).

The temperature effect on viscosity can be described by an Arrhenius type equation:

$$\eta = \eta_0 e^{-\frac{E_A}{RT}} \qquad (2)$$

where: η – dynamic viscosity (Pa.s),
η_o – the reference value of dynamic viscosity (Pa.s),
EA – activation energy ($J.mol^{-1}$),
R – gas constant (8,314472 $J.K^{-1}.mol^{-1}$),
T – thermodynamic temperature (K).

Many authors (*Hlaváč, 2011*; *Munson et al., 2009*) explain, that the temperature dependence of viscosity may be explained by cohesive forces between molecules, too. These cohesive forces between molecules decrease with increasing temperature and flow becomes freer. As a result, viscosity of liquids decreases with increasing temperature. The fluidity of liquids in liquid state can be explained by relatively weak forces of mutual activity of molecules and their high movability. The fluidity of various liquids is different, and it equals to reciprocal of dynamic viscosity:

$$\varphi = \frac{1}{\eta} \ (Pa^{-1}.s^{-1}) \qquad (3)$$

Kinematic viscosity can be defined as quotient of dynamic viscosity and density of liquids when measured at the same temperature:

$$\nu = \frac{\eta}{\rho}, \qquad (4)$$

where η is dynamic viscosity in Pa.s and ρ is density in $kg.m^{-3}$. The basic unit of kinematic viscosity is $m^2.s^{-1}$, but smaller unit $mm^2.s^{-1}$ is also commonly used (*Štěpina , Veselý, 1985*).

The fluidity is ability of matters to flow. Parts of liquid matters can move easily towards one another because the particles are not bounded in fixed positions. The measure of fluidity is expressed by viscosity. It is defined as reciprocal of dynamic viscosity (3).

Thermogravimetric Analysis was measured on METTLER TOLEDO. The temperature method of the experiment was set according to the needs of samples and conditions of laboratory. The temperature was increased from 25 °C to 200 °C at a heating rate of 10 °C.min^{-1}. Isothermal part of experiment was not occurred. After achieving the temperature 200 °C the sample was cooled to an operating temperature of 25 ° C. TGA was performed in nitroge atmosphere throughout the experiment.

As carrier gas was used nitrogen (purity 99 %). Gas flow was for both methods 50 ml.min^{-1}. The device TGA/DSC1 was employed to measure the changes of mass in the samples and to monitor the temperature processes. TGA measurement was realized in Alumina crucible with lids and with diameter of 6 mm and length of 4.5 mm. The total volumes of the crucibles were 70 µl and the lids were pierced. Simultaneously with the thermogravimetric analysis, DTA measurement was performed. The sample was weighed by scales KERN ABT 220-5DM version 1.2 03/2013 (Kern & Sohn GmbH, Balingen, Germany).

RESULTS AND DISCUSSION

Temperature dependence of dynamic viscosity was measured at temperatures ranging from 20 °C to 80 °C. The coefficients of regression equations and coefficients of determination are summarised in the Table 3. We can observe from Table 3 that dynamic viscosity of samples is decreasing exponentially with increasing temperature. It was expected and it corresponds with conclusions of fluid materials reported in literature (*Vozárová et al., 2015; Hlaváč et al., 2017, 2019, 2021; Trávníček et al., 2013*). The determination coefficients for all the samples are very high, what confirms strong exponentially decreasing dependence, too. The progress can be described by a decreasing exponential function, which is in accordance with Arrhenius equation.

Tab. 1 Dependences of dynamic viscosity on temperature

	Regression equation	Determination coefficient R^2
Cherry	$y = 3{,}2046e^{-0{,}011x}$	0,9542
Plum	$y = 3{,}1777e^{-0{,}011x}$	0,9556
Pear	$y = 3{,}244e^{-0{,}013x}$	0,9671
Peach	$y = 3{,}5286e^{-0{,}015x}$	0,981
Apricot	$y = 3{,}3763e^{-0{,}013x}$	0,9637

Tab. 2 Dependences of kinematic viscosity on temperature

	Regression equation	Determination coefficient R^2
Cherry	$y = 3{,}312e^{-0{,}01x}$	0,9442
Plum	$y = 3{,}3211e^{-0{,}01x}$	0,9459
Pear	$y = 3{,}381e^{-0{,}012x}$	0,9602
Peach	$y = 3{,}6979e^{-0{,}014x}$	0,9775
Apricot	$y = 3{,}7663e^{-0{,}015x}$	0,909

Tab. 3 Dependences of density viscosity on temperature

	Regression equation	Determination coefficient R^2
Cherry	$y = 0{,}9676e^{-9E-04x}$	0,9909
Plum	$y = 0{,}9568e^{-9E-04x}$	0,9921
Pear	$y = 0{,}9595e^{-9E-04x}$	0,9919
Peach	$y = 0{,}9542e^{-1E-03x}$	0,9949
Apricot	$y = 0{,}9543e^{-0{,}001x}$	0,9826

Tab. 4 Dependences of fluidity on temperature

	Regression equation	Determination coefficient R^2
Cherry	$y = 312{,}05e^{0{,}0111x}$	0,9532
Plum	$y = 314{,}7e^{0{,}0113x}$	0,9681
Pear	$y = 308{,}26e^{0{,}0129x}$	0,9689
Peach	$y = 283{,}4e^{0{,}0148x}$	0,9802
Apricot	$y = 278{,}81e^{0{,}0148x}$	0,9681

With the increasing temperature, the density decreased. We found out from the experimental measurement that the distillate of cherry has the highest density. It is caused by the fact that 30 - 40%

of the total weight of cherry is a stone which causes more oily substances. The lowest density was measured from the apricot, where the maximum of weight of the stone is only 10 %. The overall decrease of progress in curves is described by exponentially regressive equation. The coefficients of determination reached high values in all samples. We can conclude from the measurements that the regression equations describe very precisely graphically shown decreasing dependencies. Those results confirmed validity of Arrhenius exponential relation. We compared in the graphical dependence of density on temperature the coefficients of determination of linear model of regression equation with the coefficient of determination of exponential shape of curve. Similar comparison was made by (*Kumbár, 2013*) with stating that both measured coefficients reached high value. We can see that there is not a big difference between linear and exponential mathematical models – from mathematical point of view. On the other hand, from the physical point of view, better interpretation has exponential dependence of Arrhenius type.

Temperature dependencies of samples of dynamic viscosity had an exponential decreasing shape, which is in accordance with Arrhenius equation. Kinematic viscosity of samples is decreasing with increasing temperature. When heating the compared samples, their fluidity increases. Thermogravimetric (TG) curve, as a function of respective boiling temperature, where are quite like those obtained by TG curve of alcohol, performed in alumina pan with pinhole lids. All the samples were put into the similar mass from 93,70 mg to 115,60 mg. Fig. 1 shows the TGA results for at 200 °C with different composition (apricot, plum, peach, cherry and pear).

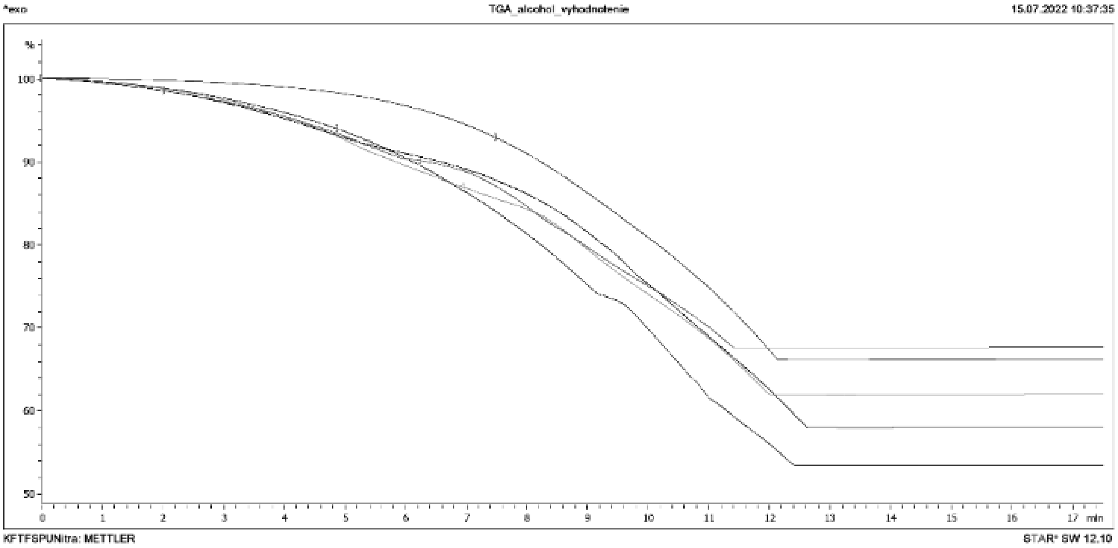

Fig.1 Thermogravimetric curves of distillate by heating rate 10 °C.min^{-1}, where blue colour is apricot, violet is plum, red is pear, black is cherry and green colour is pear distillate.

Curves are normalized and they show evident most decrease of mass by apricot and least by peach. All samples terminate yourself decreases around 150 °C. Basic information about decreases of samples are indicated in Tab. 1.

Tab. 1 Temperatures and final mass determined from analysis TG curves

	Onset (°C)	Residue (%)	Inflect. Pt. (°C)	Onset (°C)	Residue (%)	Inflect. Pt. (°C)
apricot	56.7	74.03	75.34	88.35	70.08	91.58
plum	-	-	-	85.76	91.94	102.71
peach	42.76	97.72	59.09	84.3	73.08	102.46
cherry	37.58	91.1	51.8	88	57.92	104.3
pear	43.12	87.06	55.61	92.72	61.87	103.04

TGA results show that the alcohol undergoes thermal degradation beginning around 40 °C (onset temperature), the greatest rate of change on the curve which is also known as inflection point at 102 °C and the total mass loss of 42,08 %. The residue remaining was from 57,92 % to 91,94 % at 140 °C to 150 °C. Shift of the TG curves responsible volatile melt, it is the liquid sample evaporate. All processes in this temperature range are covered by evaporation binary solution of water and ethanol.

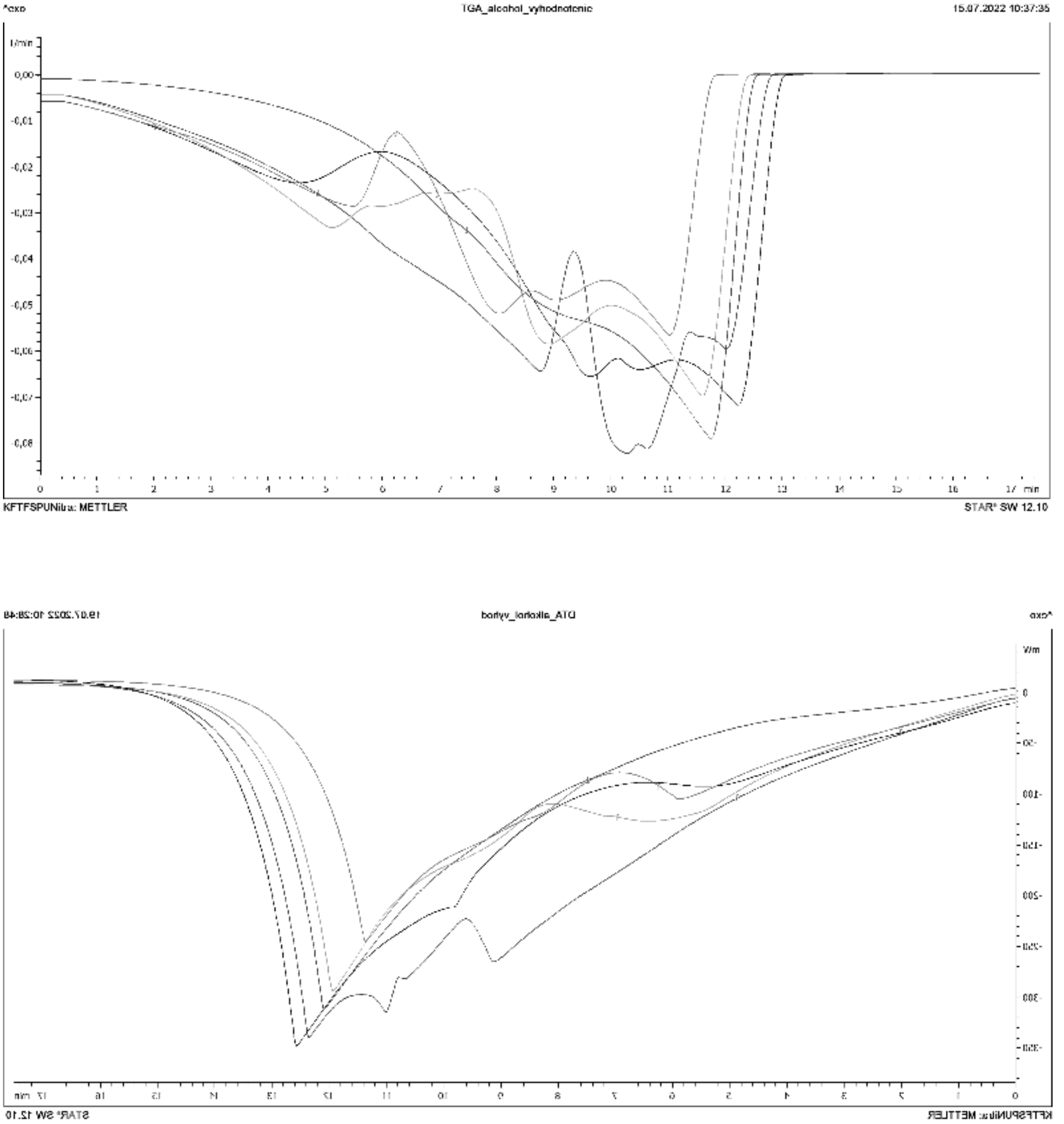

Fig. 2 DTG (left) and DTA (right) curves of distillate by heating rate 10 °C.min-1, where blue colour is apricot, violet is plum, red is pear, black is cherry and green colour is pear distillate.

To further characterize this process of samples was can the peak calculation of the 1st derivative of the mass loss curve. There is represented by DTG curves in the Fig. 2. Distinct peaks are in three samples at to temperature 55 °C (endset). Table 2 contains summary information about the individual peaks of the DTG curves. DTG curves can be divide into two parts, the first part being up to temperature 80°C and second part starting from this temperature to ending process. Peaks from first part are observable in peach, cherry and pear. It can be explained by the higher alcohol content without reaction with water and another components of distillate.

Tab. 2 Temperatures determined from analysis DTG curves

	Onset (°C)	Peak (°C)	Endset (°C)	Onset (°C)	Peak (°C)	Endset (°C)
apricot	-	-	-	63.38	103.89	120.1
plum	-	-	-	89.75	102.13	118.04
peach	35.33	59.21	66.24	74.53	101.79	111.72
cherry	31.08	50.47	62.78	86.41	103.45	121.49
pear	42.2	54.03	60.43	84.4	102.72	117.23

Main change of mass is large area of reference temperature from 80 °C to 150 °C. In peach and cherry is visible three tip at DTG curve. Two peaks are showed at temperatures (110-140) °C. One peak is observed in the plum with protracted left side peak and ending the process is determine by 149 °C. DTG curve of apricot include to the main area four peak of mass change. Peak in the main change of mass loss were match to the temperature of boil acetates. DTA curves measured concurrently with TGA as change of the heat flow determine strongly endothermic process in two curves part. One endothermic peak is visibly in firstly part of DTA curve to 80 °C in pear and peach distillate. Then follows endothermic case volatile other components of samples as aldehydes, acetates, terpenes and aromatic ingredients.

CONCLUSION

We can observe from all samples that the viscosity and density are decreasing with increasing temperature. The density and the dynamic viscosity demonstrated high temperature dependence. While distilling stone fruits, more oily substances (essential oils) are distilled and those have influence on measurement of rheological characteristics. Difference is minimal what is very suitable from the point of view of quality of distillates. The research will continue to identify tolerance limits for each distillate and based on that finding out, it will be possible to determine alcohol strength for individual produced distillate. Thermal analysis are respectable methods for analysis foods samples and alcohol. Good precondition is investigated basic composition of the samples by precisely treatment of methodology. Likeness DTA and DTG they confirm this claim. The Present peaks by temperature to 80 °C be permitted forecast change of the rheological properties (*Leonardo, 2020; Tripodi, 2022*) based on azeotropic blend water and alcohol.

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REFERENCES

1. Albertson, W.C., Staley, D.R., Mcdonald, M.M. & Pryor, B.K. 2008. Engine oil viscosity diagnostic system and methods. United States Patent 20080223114.
2. Golles, A.(2001). Ušlechtilé destiláty: Praktická kniha o pálení. Praha: Ivo Železný. 109 s. ISBN 80-237-3642-6.
3. Hagman, Klaus & ESSICH, Birgit. Pálíme ovoce. Stuttgart: VÍKEND, 2007, 95 s. ISBN 978-80-86891-66-8.
4. Hlaváč, P. (2011). Reologické vlastnosti potravinárskych materiálov : dizertačná práca. Nitra: SPU, 2011. 135 s.
5. Hlaváč, P., Božiková, M., Ardonová, & V., Kotoulek, P.(2019). Apparent viscosity and density of chosen tomato ketchups. In BPS 2019. Gödöllő: Szent István Egyetem,, s. 20. ISBN 978-963-269-823-6.
6. Hlaváč, P., Božiková, M., Regrut, T., & Ardonová, A. (2017). Rheologic properties of selected vegetable oils. In INOPTEP 2017. Novi Sad : National society of processing in agriculture. (2017), s. 137. ISBN 978-86-7520-393-3.
7. Hlaváč, P., & Hlaváčová, Z.(2021). Comparison of apparent viscosities and densities of some mustards. In BioPhys Spring

2021. Lublin: Institute of Agrophysics Polish Academy of Sciences, s. 42--43. ISBN 978-83-89969-68-2

8. Hrubá, K., & Lapčíková, B. (2018). Thermal analysis and its use in the food industry. Univerzita Tomáše Bati ve Zlíňe [internet] aviable from: http://digilib.k.utb.cz/bitstream/handle/10563/42099/hrub%C3%A1_2018_dp.pdf?sequence=1&isAllowed=y
9. Joardder (Omar), M. U.H, Karim, A., & Kumar, Ch. (2013).Better Understanding of Food Material on the Basis of Water Distribution Using Thermogravimetric Analysis. Conference: International Conference on Mechanical, Industrial and Materials Engineering 2013 (ICMIME 2013) At: RUET, Rajshahi, Bangladesh. DOI: 10.13140/RG.2.1.1508.8807
10. Krempaský, J. (1982). Fyzika. Bratislava : Alfa. 1982. ISBN 80-05-01063-X. 752 s.
11. Kumbár, V., Polcar A., & Votava, J. (2015)b. Physical and Mechanical Properties of Bioethanol and Gasoline Blends. Sugar and Sugar Beet Journal, vol. 131, no. 3, p. 112-116. ISSN 1210-3306
12. Kumbár, V., Polcar, A., & Čupera, J.(2013). Rheological profiles of blends of the new and used motor oils. Brno : Acta Universitatis Agriculturae et Silviculturae Mendelianae Brunensis,. ISSN 1211-8516, s. 115-121
13. Leonardo, R.S., Murta Valle, M.L., &Dweck, J. (2020). Thermovolumetric and thermogravimetric analysis of diesel S10. J Therm Anal Calorim 139, 1507–1514. https://doi.org/10.1007/s10973-019-08528-7
14. Lexa, D., &Leibowitz, L. (2002). Differential Thermal Analysis and Differential Scanning Calorimetry. Characterization of Materials. E.N. Kaufmann (Ed.). https://doi.org/10.1002/0471266965.com030
15. Munson, B.R., Young, D.F., & Okiishi, T.H. (2009). Fundamentals of fluid mechanics. New York:John Wiley & Sons. 783 pp.
16. Pischl J.(1997). Vyrábíme ušľechtilé destiláty. Vydavateľstvo Glos, s.r.o. 05/122. ISBN 80-237-3441-5. Leopold Stocker Verlages.
17. Škopek, J.(2003). Výroba destilátů z vlastního ovoce. 1. vyd. České Budějovice: Dona. 139 s. ISBN 80-7322-045-8.
18. Štěpina, V., & Veselý, V. (1980). Mazivá a speciální oleje. 1vyd. Slovenská akadémia vied v Bratislave : VEDA, 1980. 696 s.
19. Štepina, V., & Veselý, V. (1985). Mazivá v tribologii. Bratislava : Veda, vydavateľstvo Slovenskej akadémie vied, 1985. 408 s.
20. Thermal Analysis of Foods (2018). [internet] aviable from: http://people.umass.edu/~mcclemen/581Thermal.html
21. Trávniček, P, Valach, M., Hlaváčová, Z., Mareček, J., Vítěz, T., & Junga, P. (2013). Selected physical properties of liquid biofuels. Research in Agricultural Engineering 59(4), 121–127.
22. Tripodi, A., & Rossetti, I. (2022). Aspects of the thermogravimetric analysis of liquid mixtures as predictive or interpretation tool for batch distillation. J Therm Anal Calorim 147, 6765–6776. https://doi.org/10.1007/s10973-021-10990-1
23. Vega, D., Villar, M.A., Failla, M.D. et al. (1996). Thermogravimetric analysis of starch-based biodegradable blends. Polymer Bulletin 37, 229–235. https://doi.org/10.1007/BF00294126
24. Vozárová, V., Kardjilova, K., Híreš, Ľ., Valach, M., & Wollner, A. (2015). Temperature dependence of dynamic viscosity and DSC analysis of the Plantohyd samples. Journal of Central European Agriculture 16(2), 221–23

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