

Rheological Characterization of Liquid Raw Materials for Solid Biofuel Production

Nevena Mišljenović¹, Reidar Barfod Schüller², Elling-Olav Rukke² and Carlos Salas-Bringas¹

¹ Dep. Of Mathematical Sciences and Technology, Norwegian University of Life Sciences, P.O. Box 5003, N-1432 Ås, Norway

² Dep. Of Chemistry, Biotechnology and Food Science, Norwegian University of Life Sciences, P.O. Box 5003, N-1432 Ås, Norway

ABSTRACT

In this paper, rheological properties of different liquid and semisolid materials with high potential for usage in solid biofuel production were studied and compared. The following five materials were selected for examination: rapeseed oil, linseed oil, waste vegetable oil, palm oil and sugar beet molasses. Rheological examination was performed by shear and oscillatory tests.

INTRODUCTION

According to The European Committee for Standardization (Standard: TC335–Solid biofuels) additives in solid biofuel production are materials that improve the quality of the fuel, reduce emissions or make production more efficient¹. Those materials can be in a powder (starch, flour, lignosulfonate, etc.) or liquid form (vegetable oils, crude glycerin, molasses, etc.).

Liquid additives are added to main raw materials (sawdust, straw, grass, waste, etc.) to increase energy content, reduce energy consumption for pelleting/briquetting process, decrease dusting behavior, avoid segregation and improve the physical quality of pellets/briquettes¹⁻³. The choice of additives depends on the desired effect on fuel or process, its availability and price.

Selection of raw materials and additives for biofuel purposes should be done according to ethical principles as well. The materials that can be used in human or animal nutrition should be avoided or limited in biofuel production. Consequently, food price increasing due to bioenergy production growth will be avoided. The usage of by – products or waste from industry, agriculture or households is the best way to achieve environmentally and economically sustainable fuel production.

Vegetable oils, especially waste vegetable oil and palm oil, have high potential for usage as an additive in solid biofuel production, due to large quantities available, high calorific value, low heavy metal content and low moisture content⁴. Additionally, oil inclusion reduces energy requirements for pelleting process but, on the other hand has a negative effect on pellet durability and hardness².

When physical quality of compacted biomass (pellets, briquettes) does not meet standards or customer requirements, additional binding agents must be incorporated. Present standards for solid biofuels promote the usage of natural binders such as starch, corn flour, and potato flour in order to keep biomass fuel chemically unmodified¹. Sugar beet/cane

molasses is also known as a binding agent in production of pelleted feed or biofuel^{1, 5}. Sugar beet molasses is dark brown, viscous and sticky. It is a highly concentrated syrup ($\approx 80\%$), which is a by-product of sugar industry. Nowadays molasses is mainly utilized in fermentation processes like bioethanol production⁶, bakery yeast (*Saccharomyces cerevisiae*) production⁷ and as an additive in animal nutrition⁸. Binding properties of molasses are particularly important for pelleting of herbaceous biomasses (straw, hay, grass cutting, etc.) since pellets from those materials showed poor mechanical durability¹. Binding mechanism of molasses is based on recrystallization of soluble sugars, and consequently formation of solid bridges between particles⁹.

Rheological behavior of liquid additives are very important to evaluate its changes during different stages of production (mixing, vacuum coating, pelleting) and storing. One of the main challenges in liquid addition is how to spread the liquid evenly in a bulky powder material and avoid formation of big agglomerates¹⁰. Understanding of rheological characteristics of additives allows anticipating of different phenomena during solid biofuel production such as: spread-ability of additives in the powder mixture, flow and compactability of the powders during pelleting at different temperatures and pressures, incorporation and retention of additives in the pellet voids during and after pelleting process.

The aim of this study is to examine and compare the rheological properties of selected liquid and semisolid materials and to predict their physical behavior during different stages of solid biofuel production. This information will be used further to select the most appropriate raw materials for biofuel production.

EXPERIMENTAL PROCEDURE

Materials

The following five materials with high potential for usage in solid biofuel production were selected for examination: waste vegetable oil (WVO), rapeseed oil (RSO), linseed oil (LSO), unrefined palm oil (PO) and molasses. PO (KTC, UK) and LSO (Helios, Germany) were purchased in a local store in Norway. WVO and RSO were obtained from McDonald restaurant in Norway, Vestby. Molasses (Felleskjøpet, Norway) was obtained from the Centre for Feed Technology (FôrTek), Norwegian University of Life Sciences, Ås, Norway. Before measurements all materials were stored at 4°C.

Rheological analysis

Rheological measurements were carried out using an Anton Paar MCR301 rheometer (Austria). Oil samples (WVO, RSO, LSO) were tested using a cone-plate measuring system (cone diameter 50 mm, angle 1°, gap size 0.101 mm), while molasses and PO were tested using a bob-cup measuring system (Searle type) (cup diameter: 28.91 mm; bob diameter: 26.66mm). An overview of used measuring conditions and type of tests is given in the Table 1.

Analysis of oils (WVO, RSO, LSO)

Flow tests were conducted at constant temperature (20°C) at a shear rate range of 0.001 – 500 s⁻¹.

Rotational temperature scan was performed with the temperature changing linearly from 20 to 180°C (heating) and from 180 to 20°C (cooling), with a constant shear rate of 200 s⁻¹. Each phase (heating and cooling) lasted 20 minutes. This temperature range was chosen to cover all temperatures which are applied during solid biofuel production.

Table 1. Overview of the experimental work.

Material	Measuring system	Type of test	Temperature (°C)	Shear rate (s ⁻¹)	Angular frequency (rad/s)	Strain (%)
WVO, LSO, RSO	Cone - Plate	Rotational	20	0 - 500	-	-
WVO, LSO, RSO	Cone - Plate	Rotational	20 - 180 180-20	200	-	-
PO	Bob - Cup	Rotational	30	0 - 500	-	-
PO	Bob - Cup	Rotational	30 - 180 180-30	200	-	-
PO	Bob - Cup	Oscillatory	30 - 100 100 - 30	-	10	0.1
Molasses	Bob - Cup	Rotational	20	0-500	-	-
Molasses	Bob - Cup	Rotational	20-100 100-20	200	-	-
Molasses	Bob - Cup	Oscillatory	20 - 80 80 - 20	-	10	0.1

Analysis of palm oil

Since the PO has a solid appearance at room temperature both, rotational and oscillatory, tests were performed.

A flow test was conducted at constant temperature (30 °C) at a shear rate range of 0.001 – 500 s⁻¹. A temperature scan was performed at constant shear rate (200 s⁻¹) by a linear temperature change from 30 to 180°C and back (180-30°C).

During the oscillatory test, PO was subjected to a harmonically sinusoidal deformation with constant strain and angular frequency of 0.1% at 10 rad/s, respectively. Temperature was linearly changed from 30 to 100 °C and back (100 - 30 °C).

Analysis of molasses

A flow test was performed at a constant temperature of 20 °C, in a shear rate range from 0.001 to 500 s⁻¹. Molasses was heated in the rheometer from 20 to 100°C and cooled afterward from 100 to 20 °C. The dry matter content of molasses before and after temperature/cooling was determined using a Pallete PR-201α refractometer (Atago, Co. Ltd, Japan).

Small amplitude oscillatory scanning was performed by changing temperature from 20 to 80°C under constant strain and

angular frequency of 0.1% and 10 rad/s, respectively.

Data analysis

The effect of temperature on viscosity was described through the Arrhenius model (Eq.1):

$$\eta = A \cdot e^{-\left(\frac{E_a}{RT}\right)} \quad (1)$$

where η is the dynamic viscosity, A is a constant, E_a is the energy of activation for viscosity (J mol⁻¹), R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is the absolute temperature (K). The activation energy was obtained by plotting $\ln(\eta)$ against $1/T$. E_a and A were determined from the slope and intercept of a linear curve fit.

The power law equation (Eq. 2) was used to analyse the non-Newtonian flow behaviour of PO and molasses:

$$\sigma = K \cdot \dot{\gamma}^n \quad (2)$$

where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s⁻¹), K is the consistency coefficient (Pa s ^{n}), and n is flow behaviour index. Plot of $\log \sigma = f(\log \dot{\gamma})$ is a straight line with slope equal to n and intercept equal to $\log K$.

Accuracy of curve fitting was confirmed by coefficient of determination (R^2).

RESULTS AND DISSCUSION

On the Fig.1 are presented flow behavior characteristics of vegetable oils (WVO, RSO and LSO) examined at 20°C. Vegetable oils showed a linear shear stress - shear rate relation. Viscosity of the WVO (0.117 Pa s) was higher than viscosity of the RSO (0.076 Pa s), confirming that continuous or repeated frying increase viscosity of oil due to oxidation and polymerization reactions ¹¹.

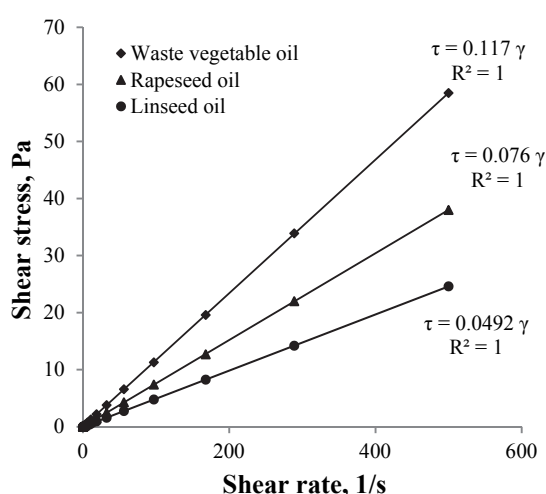


Figure 1. Flow curve of vegetable oils (WVO, RSO and LSO) at 20°C in a shear rate range from 0 to 500 s⁻¹.

In production of pelleted biofuels oils can be applied in a two way, by mixing with a main raw material (sawdust or straw) before pelleting process, or by vacuum coating technology after pelletization. Oil inclusion will decrease energy consumption for pelleting process due to lubricating effect, and also increase energy content in pellet because oils have higher calorific value compared to wood or straw. However, reduction of physical pellets quality (hardness and durability) is inevitable, so further investigation in respect to determination of optimal oil amount is necessary.

A liquid placed into a compacted solid material (pellet) provides a liquid–solid interface. Porosity of pellets and surface phenomena are critically important for oil retention in pellets. Leakage of oil will occur if gravity forces are beyond inter-molecular attractive forces between the liquid and solid surrounding surfaces and pellets are highly porous¹². Porosity of pellets depends on pressure level during the pelleting process and on compressibility of the material.

Additionally, one of the uncertainties is whether and in which extent the oil will react with extractives (lipid and phenolic nature) in sawdust and whether that interaction will be positive or negative for pellet quality.

Viscosity of oils as a function of temperature is shown in Fig. 2 (PO also presented). As the figure illustrates viscosity decreased with increasing of temperature. At lower temperatures differences in viscosity between examined oils are more visible, but after certain temperatures (around 80 °C) very small differences can be noticed.

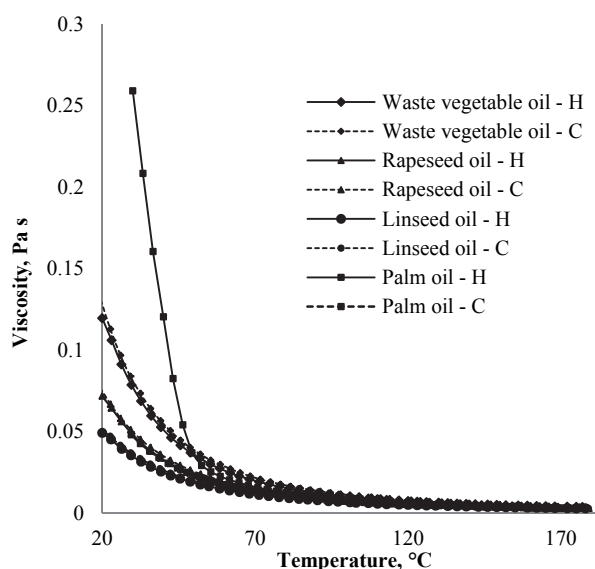


Figure 2. Viscosity change of oils during the heating (H: 20→180°C) and cooling (C: 180→20°C) at 200 s⁻¹ shear rate.

Compared to other oils PO showed different behaviour. PO has solid-like appearance when observed at room temperature. Apparent viscosity of PO at 30 °C and 200 s⁻¹ shear rate is 0.259 Pa s. The apparent viscosity of PO sharply decreased with temperature increase and after complete melting at 48°C (Fig. 4) PO showed similar viscosities to the other oils tested. However, when cooled PO does not recover its initial viscosity. WVO, RSO and LSO had almost the same viscosity during the heating and cooling. Slightly higher value of viscosity during the cooling (no complete overlapping of heating and cooling line) is a consequence of the thermal degradation of oil that occur above 80 °C¹¹. Increase in viscosity was not more pronounced because of the short residence time at high temperatures (20 minutes for each, heating and cooling).

Differences in the viscosity of the examined oils (including PO after melting point) are not large, which provides flexibility in additive choice, since the same equipment and process conditions can be applied independently of oil type. In that case, the choice of additive depends on availability and price.

Table 2. Values of parameters in Arrhenius equation.

Material	A (Pa s)	E _a (kJ/mol)	R ²
WVO	5.2·10 ⁻⁶	23.827	0.9878
RSO	7.5·10 ⁻⁶	21.707	0.9873
LSO	1.2·10 ⁻⁶	19.783	0.9900
PO ^{*_h}	5.3·10 ⁻⁶	22.910	0.9907
PO _c	6.4·10 ⁻⁶	21.968	0.9921
Molasses _h	2.3·10 ⁻⁹	53.074	0.9890
Molasses _c	1.0·10 ⁻¹⁰	61.648	0.9950

* used data after melting point; h – heating; c - cooling

The temperature dependence of viscosity is modelled by Arrhenius equation (Eq. 1). In the Table 2 are presented estimated Arrhenius model parameters for all examined materials. According to R², these

models adequately describe the influence of temperature on oil viscosity. Since the Arrhenius model is valid only for pure liquids, the values after melting point of PO were used for estimation of model parameters. Higher values of activation energy indicate a more rapid change of viscosity with temperature¹³.

Fig. 3 shows the change in the apparent viscosity of PO as a function of shear rate. Apparent viscosity of PO decreased with shear rate increase, indicating that the flow of PO is pseudoplastic. Also, hysteresis curve (thixotropic) indicates that rheological properties of PO are time dependent. After the completion of the rotational test PO had not the same viscosity as at the beginning of the test probably due to molecules reorganization and changes in the crystal structure of the material.

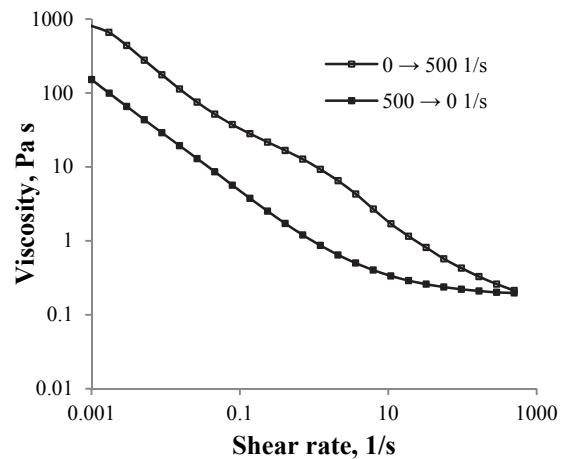


Figure 3. The relationship between the apparent viscosity and shear rate of palm oil at 30°C.

Power law model (Eq. 2) was used to describe the flow behavior of palm oil. Estimated values of consistency coefficient and behavior index are presented in the Table 3. High values of coefficient of determination (R²) indicate that power-law model was suitable for describing the flow behavior of PO. Values of *n* for PO (0.4645 and 0.3573) indicate strong shear thinning behavior.

Table 3. Power law parameters for palm oil and molasses.

Material	$\dot{\gamma}$ (s^{-1})	K ($Pa s^n$)	n	R^2
Molasses	0-500	9.90	0.964	0.9999
	500-0	8.61	0.962	0.9999
PO	0-500	8.82	0.357	0.9900
	500-0	1.83	0.464	0.9290

Results of oscillatory temperature scan of PO are presented at Fig. 4. Oscillatory temperature scan was used to determine temperature dependence of the material under flow-less conditions. G' (storage modulus) is slightly larger than G'' (loss modulus) in PO at 30°C. With temperature increasing values of both modules decreased. At 48°C storage modulus completely disappear ($G'=0$) and only the viscous component is present. This temperature is a melting point of PO. After melting point PO showed the same flow properties as the other examined liquid oils. Cooling from 100 to 30°C does not recover solid nature of palm oil ($G'=0$). Certainly, for better PO distribution in sawdust or straw mixing should be done at temperatures above melting point.

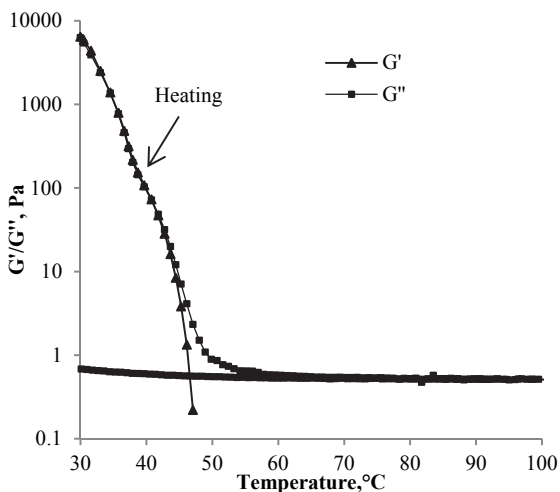


Figure 4. Storage (G') and loss modulus (G'') of PO as a function of temperature.

Fig. 5 illustrates flow behaviour characteristic of molasses. Material showed

a non-Newtonian, pseudoplastic behaviour. Apparent viscosity of molasses decreased with increasing shear rate. Power law model (Eq. 2) was used to calculate consistency index (K) and flow behaviour index (n). Values of those parameters are presented in Table 3. Values of flow behaviour index (0.964 and 0.962) confirmed pseudoplastic behaviour of molasses. Pseudoplastic characteristics are more pronounced in PO than in molasses. At Fig. 5 hysteresis curve can be observed, indicating time dependent behaviour (thixotropic) of molasses. Fig. 5 also shows that, unlike the PO properties, viscosity change of molasses was reversible, since the apparent viscosity before and after measuring was the same.

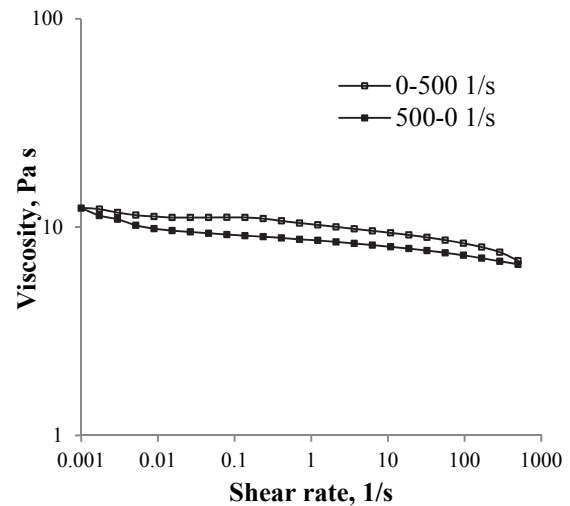


Figure 5. The relationship between the apparent viscosity and shear rate of molasses at 20°C.

Despite many advantages, usage of molasses in the pelleting process is limited mainly because of handling difficulties caused by the highly viscous and sticky nature of the molasses. One of the main challenges in the molasses application is to obtain uniform distribution of liquid in the powder mixture to avoid the occurrence of rough agglomerate. As an example, in order to avoid agglomerating in animal feed production (pelleting process), molasses is

usually diluted ($\approx 40\%$ water content) and then sprayed over agitated feed bed³. Dilution of molasses in solid biofuel production would increase water content in fuel and consequently cause some undesirable effects such as decreasing net caloric value of the fuel, reducing the maximum possible combustion temperature and increasing the necessary residence time in the combustion chamber¹⁴. Contrary, Thomas et al.⁹ stated that molasses has binding effect only in sufficient water, preferable water added in form of steam. What is the best approach for molasses application and mixing, and how it affects fuel properties can be a topic for further research.

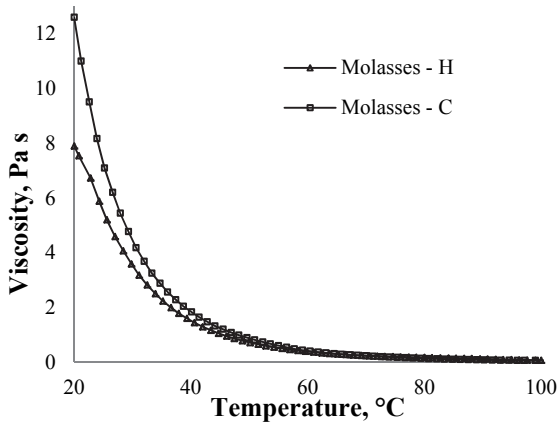


Figure 6. Viscosity change of molasses during heating (H: 20→100°C) and cooling (C: 100→20°C) at 200 s⁻¹ shear rate.

Results in this research showed that heating of molasses from 20 to 100°C reduce apparent viscosity in a great extent (Fig. 6), which is in agreement with Torgul and Arslan¹⁵. However, after cooling to 20°C molasses had higher apparent viscosity than previous measurement. Apparent viscosity of molasses after cooling was higher probably due to evaporation of water or denaturation of small amount of proteins present in molasses. Dry matter content of molasses before and after measurement was 80.8 and 84.6%, respectively, confirming that evaporation occurs during the

measurement. These findings suggest the need of mixing molasses at elevated temperatures, in an intensive mixer. Further investigations on this topic are needed.

Temperature dependence of viscosity of molasses follow Arrhenius model (Table 2). High values of E_a indicate strong influence of temperature on molasses apparent viscosity.

Fig. 7 shows the results of oscillatory temperature scan. It can be seen that the value of G'' is higher than G' . G'' of molasses decrease with increasing temperature, while the G' remains relatively constant. After cooling G'' is lower compared to initial value, while G' value was increased indicating hardening which is consequence of water evaporation.

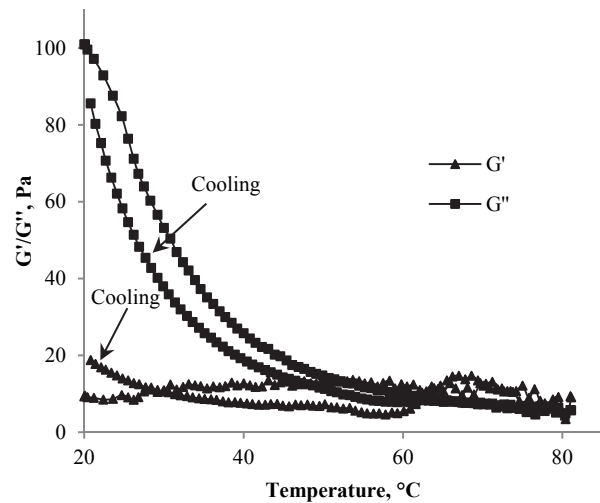


Figure 7. Storage (G') and loss modulus (G'') of molasses as a function of temperature.

CONCLUSION

The rheological characterisation of liquid additives gives useful information for their further application in solid biofuel production. Results showed that vegetable oils are Newtonian fluid, while palm oil and molasses are shear – thinning materials. Waste vegetable oil has lowest viscosity when observed at room temperature. Similar viscosities at elevated temperatures of all

tested oils provide flexibility in additive choice. Due to low nutritional value application of waste vegetable oil is preferable. Low viscosity value indicates that is possible to achieve good homogeneity by mixing waste vegetable oil with bulky materials. Molasses as binding agent can be used, but further investigation in respect to best way of its application is necessary.

REFERENCES

1. Obernberger, I. and G. Thek, (2010) "The Pellet Handbook, The Production and Thermal Utilisation of Pellets". London Earthscan
2. Kaliyan, N. and R. Vance Morey, (2009), "Factors affecting strength and durability of densified biomass products", *Biomass and Bioenergy*, **33**(3): p. 337-359.
3. Kirchner, A., A. Feil, R. Colovic, D. Vukmirovic, and J. Levic, (2013), "Discontinuous addition of small volumes of liquids in an intensive mixer to animal supplement feed with different particle size distributions", *Powder Technology*, **239**(0): p. 358-365.
4. Khalisanni, K., K. Khalizani, M. Rohani, S., and P.O. Khalid, (2008), "Analysis of Waste Cooking Oil as Raw Material for Biofuel Production", *Global Journal of Environmental Research* **2**(2): p. 81-83.
5. Thomas, M. and A.F.B. van der Poel, (1996), "Physical quality of pelleted animal feed 1. Criteria for pellet quality", *Animal Feed Science and Technology*, **61**(1-4): p. 89-112.
6. Sarka, E., Z. Bubnik, A. Hinkova, J. Gebler, and P. Kadlec, (2012), "Molasses as a by-Product of Sugar Crystallization and a Perspective Raw Material", *Procedia Engineering*, **42**(0): p. 1219-1228.
7. Razmovski, R. and V. Vučurović, (2012), "Bioethanol production from sugar beet molasses and thick juice using *Saccharomyces cerevisiae* immobilized on maize stem ground tissue", *Fuel*, **92**(1): p. 1-8.
8. Karamitros, D., (1987), "Sugar Beet Molasses for Growing and Fattening Pigs", *Animal Feed Sciences and Technology*, **18**: p. 131-142.
9. Thomas, M., T. van Vliet, and A.F.B. van der Poel, (1998), "Physical quality of pelleted animal feed 3. Contribution of feedstuff components", *Animal Feed Science and Technology*, **70**(1-2): p. 59-78.
10. Ax, K., H. Feise, R. Sochon, M. Hounslow, and A. Salman, (2008), "Influence of liquid binder dispersion on agglomeration in an intensive mixer", *Powder Technology*, **179**(3): p. 190-194.
11. Santos, J.C.O., I.M.G. Santos, and A.G. Souza, (2005), "Effect of heating and cooling on rheological parameters of edible vegetable oils", *Journal of Food Engineering*, **67**(4): p. 401-405.
12. Gilleo, K.B., (2006) "Rheology and Surface Chemistry", 3 ed, Coatings Technology Handbook, ed. A.A. Tracton: CRC Press
13. Steffe, J.F., (1996) "Rheological Methods in Food Process Engineering". East Lansing, Michigan: Freeman Press
14. van Loo, S. and J. Koppejan, (2008) "The Handbook of Biomass Combustion and Co-firing". London: Earthscan
15. Toğrul, H. and N. Arslan, (2004), "Mathematical model for prediction of apparent viscosity of molasses", *Journal of Food Engineering*, **62**(3): p. 281-289.