

Determination of Castor Oil Molecular Weight by Vapour Pressure Osmometry Technique

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Nowadays, the molecular weight of vegetable oil is usually determined by gas chromatography analysis (GC) because this analysis permits the calculation of the fatty acid composition of the vegetable oil. This work presents a method to measure the molecular weight of castor oil using vapour pressure osmometry technique (VPO) and compares the result with GC analysis and with data present in the open literature. The VPO and GC results found were 927.88 g/mol and 928.31g/mol, respectively. The molecular weight of castor oil is 927 g/mol according to literature, therefore the VPO can be a powerful measurement technique. VPO presents an accurate and fast way to measure the molecular weight of vegetable oil.

1. Introduction

Vapor pressure osmometry (VPO) is a technique used to measure the total osmolality of physiological fluids and to determine the average molecular weight of polymers in aqueous or organic solutions. This technique is described in ANSI/ASTM D 3592-77. According to the standard, the technique is applicable to all polymers that dissolve completely without reaction or degradation within a molecular weight range of between 10.000 and a lower limit that is determined by the requirement that the solute have negligible vapor pressure (Sabadini et al., 1996; Knauer, 2007).

Because of its simplicity and low cost, VPO is used extensively to determine the molecular weight (Mw) of asphaltenes and bitumen (Acevedo et al., 2005). The VPO technique enables the measurement of an "absolute" value for the average molecular weight (Mn). When used for weak or non-polar low-molecular-weight compounds, such as resins and crude oils, the technique gives accurate values similar to those obtained by mass spectroscopy (Yang and Eser, 1999).

Castor oil is a non-traditional raw material used for the production of biodiesel. This vegetable oil is comprised almost entirely (90%wt) of triacylglycerols of ricinoleic acid in which the presence of hydroxyl group at C-12 imparts several unique chemical and physical properties. Thus castor oil and its derivatives are completely soluble in alcohols at room temperature (Kulkarni and Sawant, 2003). Cvengros et al. (2006) showed that the hydroxyl group of ricinoleic acid affects some castor oil biodiesel properties such as density and viscosity. Biodiesel is a fuel made from vegetable oils,

animal fats and microbial oil (Garnica et al., 2009; Da Silva et al., 2010). The raw materials are converted into biodiesel through a chemical reaction involving alcohol and a catalyst.

The molecular weight is calculated by the relationship between two constants: the substance of reference (primary standard) and the substance of which the molecular weight will be determined. The specification of the molecular weight of vegetable oil is important for the biodiesel production process because the determination of the quantity of reactants (alcohol) is calculated according to the molecular weight of the vegetable oil. The molecular weight of vegetable oil is normally, determined by GC. This work presents a comparative study of the castor oil molecular weight determination by GC and VPO analyses.

2. Methods of Analysis

2.1 Gas Chromatography

The composition of the raw material was determined by gas chromatography equipment equipped with a flame ionization detector and with a DB 23 column. Firstly, the ethyl esters were obtained using 1%wt of sodium hydroxide (Synth) and ethanol (Merck). The reaction was carried out at 70°C with a reaction time of 20 minutes. This time permitted 98% of biodiesel conversion. After the reaction, the excess of ethanol was evaporated under a vacuum using a rota-evaporator. Then, the ester and glycerol layers were separated in a separator funnel, and the ethyl ester layer was purified. In order to remove the residue from the raw materials and the catalyst, the ester layer (biodiesel) was washed and neutralized with distilled water and phosphoric acid. After that, the esters were dried with anhydrous sodium sulfate (Synth). Then 0.1 ml of biodiesel was diluted to 10 ml using n-heptane (HPLC-grade, Merck). After that, the sample was filtered using PTFE filter (polytetrafluorethylene). Finally, the sample was analyzed in a HP gas chromatograph model STAR 3600CX (Lexington, MA) equipped with a mass spectrometry and with a HP5 column (30 m x 0.320 mm, J&W Scientific, Folsom, CA). Injector and detector temperatures were set at 250°C and 300°C, respectively. The carrier gas used was helium at 46 mL/min. Air and hydrogen flow rates were 334 and 34 mL/min, respectively. The program of the oven temperature was as follows: starting at 50 °C for 2 min; from 50°C to 180°C at 10°C/min; 180°C was held for 5 min; from 180°C to 240°C at 5°C/min. Identification of different fatty acid ethyl esters (FAEEs) was based on a reference standard, supplied by Sigma-Aldrich (St. Louis, MO).

2.2 Vapor pressure osmometry

The VPO measurements were performed at 60°C in a Knauer instrument model K-7000. This piece of equipment was designed to measure the total osmolality of physiological fluids exactly and to determine the average molecular mass of polymers in aqueous or organic solutions (Knauer, 2007).

Two thermistors are part of a Wheatstone bridge shows Figure 1 (Löser Messtechnik, 2011). Differential measurements of currents due to temperature differences at the thermistors are accomplished. The thermistors are located in a cell where the gas phase is saturated with solvent vapour. The cell temperature is electronically controlled and

maintained with an accuracy of $\pm 1 \cdot 10^{-3} \text{ }^\circ\text{C}$. One drop of the same pure solvent located on either thermistor represents a zero temperature difference or equilibrium of the measurement system (Knauer, 2007).

The vapour pressure of any solution containing solutes is lower than the vapour pressure of a pure solvent. Hence, replacing one drop of pure solvent with one drop of a solution leads to a vapour pressure difference between the two droplets. This difference however is compensated as follows: some vapour of the pure solvent that saturates the gas phase condenses on the droplet of the solution until the vapour pressures are balanced. The increasing vapour pressure of the solution droplet leads to an increase of temperature. Once equilibrium is reached, a constant measurement value is achieved.

This particular ΔT between the thermistors is always proportional to the number of particles or number of moles dissolved in the solution. Thus, either concentrations or the molecular weight can be determined; in the latter case however only if sample concentration are known (Knauer, 2007).

Benzil ($M_w = 210.23 \text{ g/mol}$) was used as standard or calibrating substance, and the solvent was toluene. Some solutions with benzil in toluene and castor oil in toluene were prepared. Then, the VPO of these solutions were determined and two regression curves were built up for the standard data and castor oil data. The measurements were repeated three times. The slope of the regression curves may pass through the graphs origins and the M_w is determined by the ratio between the coefficients of the standard (K_{St}) curves and the sample curve (K_{Sample}).

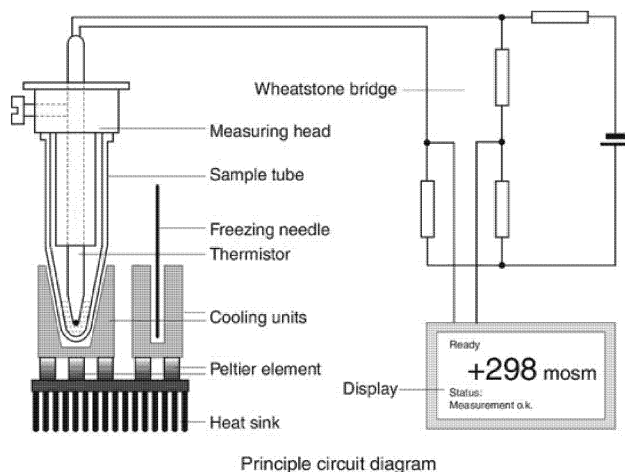


Figure 1: Diagram of osmometer

3. Results and Discussion

3.1 Gas chromatography

Table 1 shows the fatty acid content of the castor oil. The castor oil molecular weight (M_w) was calculated using equation (1), according to Filleires (1995) and Halverson (1993):

$$M_{W_{tri}} = 3.M_{W_{FFA}} + M_{W_{gly}} - 3.M_{W_{water}} \quad (1)$$

Where $M_{W_{tri}}$ is the castor oil molecular weight, $M_{W_{gly}}$ is the glycerol molecular weight, $M_{W_{FFA}}$ is the average of the free fatty acid molecular weight and $M_{W_{water}}$ is the water molecular weight.

Table 1: Fatty acid composition

Fatty acid	16:0	18:0	18:1	18:1 ^a	18:2	18:3	20:0	22:0
Molecular weight	256.4	284.5	282.5	298.5	280.5	278.5	312.5	340.6
(wt. %)	1.6	0.9	3.0	89.5	3.7	0.4	0.3	0.6

Palmitic (16:0), Stearic (18:0), Oleic (18:1), Ricinoleic acid (18:1^a), Linoleic (18:2), Linolenic (18:3), Arachinic (20:0), Behenic (22:00)

The castor oil molecular weight is $M_{W_{tri}} = 928.30$ g/mol

3.2 Vapor pressure osmometer

The VPO of five standard solutions (benzil) had concentrations from 0.025 Kg/mol to 0.1263 Kg/mol, Figure 2 shows the standard VPO results. The straight line depicts a proportional relationship between the measuring value (Mv) and the concentration ($y = K_{St} * x$). Figure 3 shows the regression curves of sample ($y = K_{Sample} * x$).

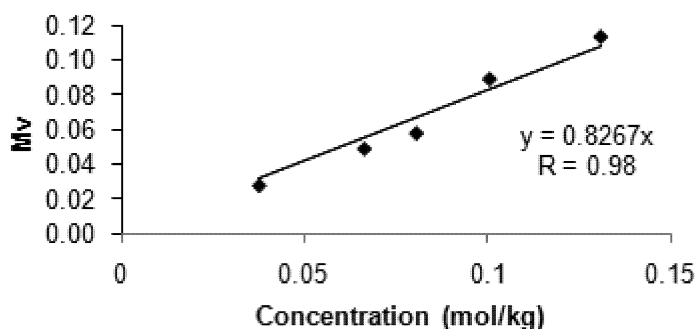


Figure 2: Calibration graph of benzil

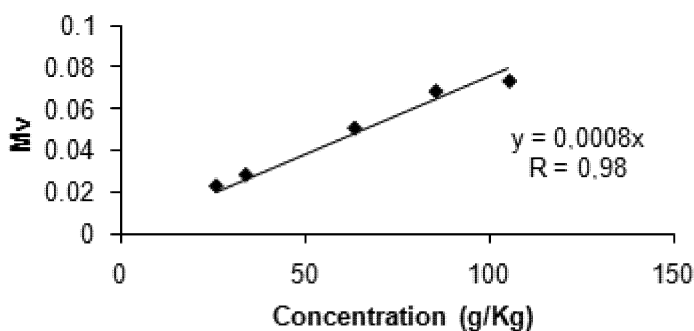


Figure 3: Castor Oil VPO analyses

The castor oil molecular weight was calculated by the ratio between the K_{St} (regression coefficient of benzyl) and K_{Sample} (regression coefficient of castor oil), as shown in the following equation (2) and this corresponded to 928.88 g/mol.

$$M_W = \frac{K_{St}}{K_{Sample}} \quad (2)$$

The molecular weight of castor oil according to Bockisc (1998) is 927g/mol, and therefore this result was close to the result published in the literature.

4. Conclusions

The determination of the molecular weight of vegetable oil is important for biodiesel production reactions because the quantity of reagents is calculated according to the molecular weight of the vegetable oil. Measuring the molecular weight by vapor pressure osmometer is an alternative method with lower cost than CG analyses.

5. References

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