Viscosity of Vegetable Oils in Methyl Ethyl Ketone and Tetrahydrofuran

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The transesterification of vegetable oil can be accelerated when conducting in single phase because it eliminates the mass transfer control. The size of the alkyl group of triglyceride can affect the reaction rate in this region since larger (bulky) alkyl group hinders another reactant methanol from approaching the ester bond. Viscosity of a solution is a convenient method to indirectly estimate the size of the solute in the solution. The current work investigates the viscosity of the solutions with different vegetable oil concentrations in two solvents, i.e., methyl ethyl ketone and tetrahydrofuran. The Huggins equation has been then applied to determine the intrinsic viscosity and the Huggins constant which are related to the size of the solute and the intermolecular interaction of solute in the solution, respectively. According to the results, intrinsic viscosities of vegetable oils increase following the order coconut oil (CO), sunflower oil (SF), and palm oil (PO). However, the intermolecular interaction is following the reverse order. This result is in accordance with our previous research on the relationship between molecular weight of triglyceride and its transesterification reaction rate in methyl ethyl ketone.

Key Words
Vegetable oil, Viscosity, Hydrodynamic size

1. Introduction
Transesterification is an important reaction for converting lipids and fats (triglycerides) to fatty acid methyl ester, so-called biodiesel oil 1. Ma and Hanna 2 compared four representative methods to convert triglycerides to biodiesel fuel: blending, microemulsion, thermal cracking and transesterification, and concluded that transesterification is the most promising method, in which the lipids are transesterified with methanol catalyzed by a catalyst, typically homogeneous alkaline.

There are numerous researches on lipid transesterification in various manners including the type of catalyst, reaction medium, and energy supply method. Catalysts include non-catalyst 3, acid or base homogeneous 4, enzyme 5, and solid 6. Reaction media include ionic liquid 7 and supercritical fluid 8. Energy supply methods include microwave 9 and ultrasonic 10, as well as conventional conductive heat-up.

Boocock et al. (1996, 1998) carried out transesterification of a few types of lipid with methanol in homogenous phase by using tetrahydrofuran (THF) as a co-solvent 11, 12. In 2016, the reaction rates of transesterification of three types of lipid, coconut (CO), palm (PO) and sunflower (SF) oils, with methanol were measured directly in homogenous phase catalyzed by potassium hydroxide at 20-60 °C using methyl ethyl ketone (MEK) as a co-solvent 13. The results showed a relationship between average molecular size of oils (lipid) and reaction rate. It means that the size of the lipid molecular can affect the reaction rate.

Viscosity of oil-solvent mixtures have been the subject of many studies such as extraction of soybean oil 14, the viscosity behavior of fatty acid esters 15, effect of temperature on viscosity 16, etc. It is found that intrinsic viscosity is a reflection of steric interferences molecular in solvent and a representative for equivalent hydrodynamic sphere of the macromolecular 17 which is the oil in this case.

As previously discussed, the transesterification rate may be related to the size of oil molecule which is reflected by intrinsic viscosity. However, there is no research on this relationship based on the authors’ investigation. Hence, the objective of this research is to investigate the viscosity of different oils in solvents and the relationship between intrinsic viscosity and the reaction rate obtained from the previous investigation 13.
2. Experimental

Experiments were conducted using a capillary viscometer for three oils (palm oil, sunflower oil, coconut oil) in two solvents (MEK and THF). Refined, food-grade cooking oils (>93% triglyceride): Country Farm brand coconut oil, Seri Murni brand palm olein and Krytsal brand sunflower oil were purchased from local stores. Analytical grade chemicals THF and MEK (99.8%) were purchased from R&M Chemicals. Different concentrations of oils in these solvents were prepared from 0 to 25 wt%. The exact concentrations are 0, 5, 7.5, 10, 25 wt%. Inverse flow capillary viscometers (No. 75 and 100) were used depending on the viscosity range of each sample. The viscometer containing samples were incubated in the water bath at 20°C for 10 min before the measurement.

Densities of these solutions were measured using SVM-3000 (Anton Parr) for later conversion of concentration and dynamic viscosity calculation.

3. Results and Discussion

Fig. 1 shows the relationship between relative viscosity and concentration of oil in MEK solvent for three types of oils, i.e., PO, SF, and CO. The non-linear regression was conducted and shows that their relationship followed quadratic equations. This relationship is consistent well with the theory of viscosity mentioned by Bovey et al. as described in equation (1).

\[
\eta_{sp} = \eta_r - 1 = [\eta]c + k' [\eta]^2 c^2
\]  

(1)

where \( \eta_r \) is the relative viscosity, solution viscosity divided by pure solvent viscosity (dimensionless), \([\eta]\), the intrinsic viscosity, is a measure of the effective hydrodynamic volume of the solute (ml/g), the Huggins constant, \( k' \), is related to intermolecular interaction (dimensionless) \((1)\). \( c \) is the concentration of oil in solvent (g/ml).

Similarly, the results of relative viscosity of these oils in THF was measured and plotted in Fig. 2, and they also followed the similar trend as in MEK.

The intrinsic viscosity and Huggins constants can be extracted based on fitting the equation (1). They are summarized in Table 1. According to the results, the intrinsic viscosity increases by the following order: CO, SF, and PO, which has a similar order with the molecular weight of these oils, i.e., 658, 877, and 851 g/mol, respectively. Moreover, the difference between intrinsic viscosity of PO and SF is very small compared to that of CO when dissolving in MEK.

When comparing the reaction rates of these oils in MEK from our previous report, the similar trend was observed. The reaction rates at 35°C were 5.02, 5.08, and 11.77 (L mol⁻¹ min⁻¹) for PO, SF, and CO, respectively. Further observation was also conducted for PO, SF and CO at 50°C (i.e., 9.93, 11.65 and 18.73 L mol⁻¹ min⁻¹), and the results also showed a similar relationship between reaction rate and intrinsic viscosity of oils in the solvent. From the present study, it was found that difference of the transesterification of reaction rate among three different oils in MEK can be attributed to bulkiness of alkyl group, which has a steric hindrance effect on methanol’s approach to the ester bond of triglyceride, the reaction site.

It is worthwhile to mention that the intrinsic viscosity of each oil in MEK is smaller than that in THF. This implies that different type of co-solvent may result in a different transesterification reaction rate. If the bulkiness is the primary hindrance factor, THF may give a smaller transesterification rate than MEK. On the other hand, if the intra-alkyl void fraction is the primary factor, THF may show a higher reaction rate than MEK.
4. Conclusion

The viscosity of three types of triglyceride in two types of solvent was investigated. Firstly, the intrinsic viscosity of triglyceride solution which is proportional to the hydrodynamic size became larger when the size of the alkyl group of the triglyceride is bigger regardless of solvent type. Secondly, the intrinsic viscosity in THF was larger than that in MEK. This exhibits better affinity between the alkyl groups in triglyceride and THF than MEK. Combining the first finding with our reaction results 13), the bulkiness of triglyceride may hinder methanol’s approach to the reaction site (ester bonds of triglyceride), and consequently lower the rate of transesterification in homogeneous phase. The possibility of using intrinsic viscosity to estimate the transesterification rate among different oils in the supporting of co-solvent was implied.

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