



Original research

Rheological properties of Babolsar sugarcane syrup

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ABSTRACT

Investigating the physicochemical and rheological properties of sugar syrups is important in specifying their usage in the food and beverage industries. In this study, some of the physicochemical properties of sugarcane syrup (72 °Brix at 25 °C), including specific gravity, ash content, sugar content, soluble solids content, acidity, and pH were determined. Results showed the following average values: 4.266 for specific gravity, 1.4% for ash content, 57.25 (g/100 g) for sugar content, 77.8 (g/100g) for soluble solids content, 0.32% (Glycolic acid) for acidity, and 4.88 for pH. The rheological properties of sugarcane syrup were also measured using a rotational viscometer at three temperature levels (25, 45, and 65 °C) and concentrations of 35, 55, and 72 °Brix. The power-law model describes well the rheological behavior of sugarcane syrup. According to the results based on Mitchka method, sugarcane syrup is a non-Newtonian, shear-thickening (Dilatants) fluid. The consistency coefficient (k) varied between 2075.58 and 194852.86 Pa sⁿ. Furthermore, the dependence of the consistency coefficient on temperature was evaluated by the Arrhenius equation, and the activation energy was found between 23695.75 to 42402.93 KJ/mol. Finally, the relationship between the consistency coefficient and concentration was evaluated using the exponential model ($R^2 = 0.9925$).

Keywords: Sugarcane syrup; Rheological properties; Power-law model; Mitchka method; Activation energy

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1. Introduction

Sugarcane is a perennial plant native to Asia. It has an aerial stem with a height of 2-6 meters, in the form of cylindrical straw with numerous nodes full of sweet liquid, containing 13-15 percent of sucrose. Sugarcane (*Saccharum officinarum* L.) is a tall plant of *Tripidium Ravennae* genus (*Saccharum Ravennae*), belongs to the *Poaceae* family, and is native to warm to tropical regions. The stalks of sugarcane plant contain lots of sugar (Papini-Terzi et al., 2009; Asikin et al., 2017).

Historically, the first attempt for sugarcane cultivation in Khuzestan was done in 1937 to 1939 but some problems such as the world war caused a lack of attention to this issue. In 1951, the sugarcane planting in Khuzestan started with the cooperation of FAO, and continued up to now, so the program of sugarcane development is one of the largest national plans of Iran. In 1986, the cropping area of this product has been around 28000 hectares

with an average operation of 83 tons of stems in hectare (Agha Farmani et al., 2006; Eggleston et al., 2002).

The planting of sugarcane begins in April, and after eight months in early January, the products will harvest. For marketing, the harvested sugarcane is sent to traditional factories, and after cleaning, sugarcane juice is extracted. The extracted liquid is poured into a dish, placed on a fire, and stirred for a long time (between 6 to 8 hours), so more than 90 percent of its water is vaporized, and a brown foam forms on its surface. The foam is removed, and a dark syrup named “Doshab” remains. “Doshab” or the dark syrup is heated constantly and stirred frequently until the light or dark brown sugar forms. Then, the produced early sugar is poured into a mold and put in a cold place to get thick (Agha Farmani et al., 2006; Silvia et al., 2006).

So far many studies had been conducted in the field of evaluation of rheological properties of different syrups, considering different temperatures and concentrations. Arslan et al. (2005) measured the rheological properties of tahin/pekmez (sesame

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paste/concentrated grape juice) blends in different concentrations of tahin (20 to 32%) and different temperatures (35 to 65 °C) using a rotational viscometer. All samples showed non-Newtonian, pseudoplastic behavior at all temperatures tested. Using the power-law model, the flow behavior index (n) and consistency coefficient (k) of samples varied between the ranges of 0.7-0.85 and 282-2547 mPa sⁿ, respectively. Although the temperature had a significant effect on both parameters, the influence of temperature on the flow behavior index (n) didn't follow the Arrhenius equation. The range of 13.376-28.592 KJ/mol was reported as activation energy, elevated with increasing tahin concentration. The effect of concentration on the consistency coefficient was determined by the exponential equation (Arslan et al., 2005).

Alpaslan and Hayta (2002) studied the rheological properties of mixtures of pekmez (grape molasses)/ tahin (sesame paste) at three different pekmez concentrations (2, 4, and 6% pekmez) and different temperature levels (30, 40, 50, 60, 65, and 70 °C). According to this study, samples showed pseudoplastic behavior and the power-law model well suited the apparent viscosity rotational speed data (Alpaslan & Hayta, 2002). Yoğurtçu and Kamişlı (2005) studied rheological properties of some Turkish pekmez samples at 5, 10, 15, 20, and 30°C using a rotational viscometer. All samples were found to show non-Newtonian behavior. According to the power-law model, all considered pekmez samples regarded as pseudoplastic fluids (Yoğurtçu & Kamişlı, 2005). In another study, concentrated date syrup has been used for increasing the nutritional properties of dairy products. The concentrated syrup from three date varieties (Khllass, Sukkari, Nubotseit) had a concentration of 72.28 °Brix. By investigating the rheological properties, it was evident that this mixed syrup was non-Newtonian and had pseudoplastic behavior (Alhamdan, 2002). Yosefzadeh Sani et al. (2018) evaluated rheological properties of watermelon juice as affected by concentration. Their results showed the temperature and concentration completely affect the rheological properties of Iranian watermelon juices.

Sugarcane syrup is considered a rich carbohydrate and nutritious food. The carbohydrates of this syrup consisted of sucrose and inverted sugars. The syrup also contains minerals such as calcium, potassium, iron, sodium, phosphorus, magnesium, and chlorine. Natural antioxidants and vitamins are other nutrients in sugarcane syrup. Regarding these properties, sugarcane syrup is considered a nutritious and energetic food (Abdel-Aleem, 2020). Sugarcane syrup regarded as a precious primary product of the sugar industry is used as a raw material in the food and beverage industries, and also for consumer use (Asikin et al., 2017). Cane syrup is sold for use on biscuits, pancakes, and cereals (Clarke, 2003).

In many food industry operations (e.g., pumping, heating, cooling, etc.), the knowledge of fluid rheology can be helpful for better management of processes and gaining good quality end products. To the best of our knowledge, despite many studies conducted on different kinds of syrups, there is a lack of research on the rheological behavior of sugarcane syrup produced in Iran. So, this study aimed to determine some of the physical, chemical, and rheological properties of sugarcane syrup.

2. Material and Methods

2.1. Materials

The sugarcane syrup (72 °Brix) was acquired from a factory in the Bahnamir district, in Babolsar, Mazandaran province, Iran.

2.2. Sample preparation

To remove the crystals and bubbles affecting syrup viscosity, samples were placed on a heated bath (Mettler, Germany) at 55 °C for an hour. After dissolving glucose crystals and to ensure complete removal of air bubbles, samples were poured into glass dishes of 0.5 L and kept in a refrigerated incubator (Binder GmbH, Germany) for 48 hours at 30 °C. An Anton Paar rotational viscometer (model Dv-3p, made in Ostrich, Germany) and a hand-held Refractometer (Atago, made in China) were used to determine the rheological properties and concentration (°Brix) of the sugarcane syrup samples, respectively.

2.3. Physicochemical properties

Some of the physicochemical properties of sugarcane syrup, including specific gravity, ash content, sugar content, soluble solids content (hand-held Refractometer, Atago, made in china), pH value (pH meter model Labor Technique), and acidity, were determined using common standard methods (AOAC, 2000).

Specific gravity was determined using the pycnometer method. For this purpose, the weight of the empty and dry pycnometer, the pycnometer full of distilled water, and the pycnometer full of sugarcane syrup were measured. Specific gravity at 20 °C was calculated using Eq. 1:

$$SG = \frac{W_f - W_0}{W_w - W_0} \quad (1)$$

where SG is specific gravity (dimensionless), W_0 is the weight of the empty pycnometer (g), W_w is the pycnometer weight full of distilled water (g), and W_f is the weight of pycnometer full of sugarcane syrup (g).

2.4. Rheological properties

The rheological properties of samples were determined at three temperature levels (25, 45, and 65 °C) and three levels of concentration (35, 55, and 72 °Brix) using a rotational viscometer (Anton Paar rotational viscometer, model Dv-3p, made in Ostrich, Germany). The viscometer spindles R_2 to R_5 were used for viscosity measurement of sugarcane syrup. The viscosity and the torque of each sample were measured after 1 min in different courses at speed of 100-250 rpm, and 10 points.

2.5. Mathematical calculations of rheological parameters on the basis of Mitchka method

This study was conducted using a single-cylinder rotational viscometer, and the power-law model based on the Mitchka method was used to calculate the rheological parameters of sugarcane syrup. The flow behavior index (n) was calculated using Eq. 2:

$$M = K'N^n \quad (2)$$

where M is torque percent or maximum torque percent registered at viscosity measurement test at a constant speed, N is

the rotational speed (viscometer spindle cycle) based on cycle in a minute (rpm), n is the flow behavior index in the power-law fluids (dimensionless), and K' is the constant of the equation. After taking the logarithm of both sides, a linear equation is obtained as follow:

$$\ln M = \ln K' + n \ln N \quad (3)$$

Consequently, the average shear stress is calculated from Eq. 4:

$$\sigma_a = K_\sigma \times C \times (\% M) \quad (4)$$

In which σ_a is the average shear stress (Pa), K_σ is the shear stress correction factor, that is a function of spindle's number (Table 1), and C is a dimensionless constant, depending on total torque capacity of the system obtained by Eq. 5:

$$C = \frac{M_{\text{Max}} \text{ (dyn.cm)}}{7187} \quad (5)$$

The average shear rate is calculated according to the following equation:

$$\dot{\gamma}_a = K_\dot{\gamma} \times N \quad (6)$$

In which $\dot{\gamma}_a$ is the average shear rate, and $K_\dot{\gamma}$ is the shear rate correction factor, dependent on the flow behavior index, obtained according to Eq. 7:

$$K_\dot{\gamma} = 0.263 (1/n)^{0.771} \quad (7)$$

In the Mitchka method, in the first place, the flow behavior index (n) is achieved by linear regression of equation (3), and then the average shear stress and the average shear rate are calculated by equations (4) and (6). The flow behavior index (n) and the consistency coefficient (k) are obtained from the power-law fluid equation (Eq. 8) by regression analysis of rheological parameters (Steffe, 1996).

$$\sigma = k\dot{\gamma}^n \quad (8)$$

2.6. Effect of temperature on consistency coefficient

The Arrhenius equation is used for evaluating the variation of viscosity with temperature (Eq. 9).

$$k = K_{0T} \exp (E_a / RT) \quad (9)$$

where k is the consistency coefficient, K_{0T} is the Arrhenius stability (Pa sⁿ), E_a is the activation energy (KJ/mol), T is the temperature (°K), and R is the universal gas constant (8.314×10⁻³ KJ/ mol K).

2.7. Effect of concentration on consistency coefficient

Comparison of variation of viscosity with concentration is another parameter evaluated following the exponential function (Eq. 10).

$$k = K_{0C} \exp (BC) \quad (10)$$

where K_{0C} is the pre-exponential constant, C is the concentration, and B is a coefficient.

2.8. Statistical analysis

The samples were tested at three replications. Analysis of physicochemical properties, evaluation of rheological models, and the linear regression analysis were done using Microsoft Excel 2010.

Table 1. The shear stress correction factor (k_σ).

Number of Spindle	k_σ
1	0.035
2	0.119
3	0.279
4	0.539
5	1.05
6	2.35
7	8.40

Table 2. Some of physicochemical properties of sugarcane syrup (Temperature 25 °C, concentration 72 °Brix).

Physicochemical properties	Value
Specific gravity (dimensionless)	4.266
Ash (%)	1.4
Sugar content (g/100g)	57.25
Soluble solid content (g/100g)	77.8
pH	4.88
Acidity (Glycolic Acid %)	0.320

3. Results and Discussion

3.1. Physicochemical properties

The physicochemical properties of sugarcane syrup evaluated in this study (Table 2) agreed with the properties of other kinds of syrups (Golafshani & Tavakolipour, 2008; Batu, 2005). For example, the pH of sugarcane syrup is obtained at 4.88 which is similar to 4.9 reported by Batu (2005) as the pH of pekmez and 4.65 reported by Mohammadzadeh Milani et al. (2019) as the pH of the fresh white grape molasses. The sugar content of sugarcane syrup is obtained at 57.25 (g/100g) similar to 64.13% reported by Simsek et al. (2004) as the sugar content of pekmez and 65.38% reported by Mohammadzadeh Milani et al. (2019) for grape molasses. Tavakolipour and Kalbasi Ashtari (2013) reported the physicochemical values of grape molasses (76 °Brix, 25 °C) as follows: 1.389 for specific gravity, 1.803% for ash, 62.68 g/100g for total sugar, 77.477 g/100 g for total solids content, 4.755 for pH, and 0.440% tartaric acid for acidity. Common commercial syrups contain 73% or 76% solids (Clarke, 2003). According to the UNICAMP (2011), the ash content of sugarcane syrup is 1.3 g/100g (UNICAMP, 2011). Vicentini-polette et al. (2019) evaluated the physicochemical properties of fifteen brands of sugarcane syrup and reported the following average values: 4.7 for pH, 0.70% total acidity, 81.9% total solids, and 1.6% ash.

3.2. Rheological properties

3.2.1. Mitchka method

The evaluation of sugarcane syrup rheological properties at three temperature levels (25, 45, and 65°C) and three levels of concentration (35, 55, and 72 °Brix) showed that all samples were non-Newtonian fluids, and the power-law model was well fitted for this syrup. Sugarcane syrup showed shear-thickening behavior. According to the results, at constant shear speed, the shear stress decreased as the temperature increased. The shear-thickening behavior of sugarcane syrup is evidenced by the logarithm plots of torque versus rotational speed (Fig. 1-3), by a linear gradient of the flow behavior index, and also considering rheogram of shear rate versus shear stress (Fig. 4).

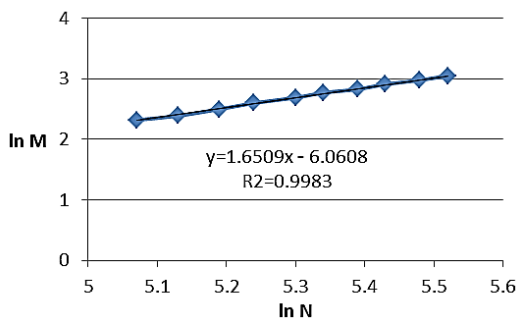


Fig. 1. A logarithmic plot of torque (M) vs rotational speed (rpm) (N) for the sugarcane syrup at concentration of 35 °Brix and temperature of 25 °C.

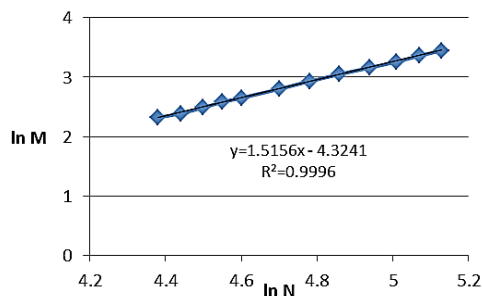


Fig. 2. A logarithmic plot of torque (M) vs rotational speed (rpm) (N) for sugarcane syrup at concentration of 55 °Brix and temperature of 25 °C.

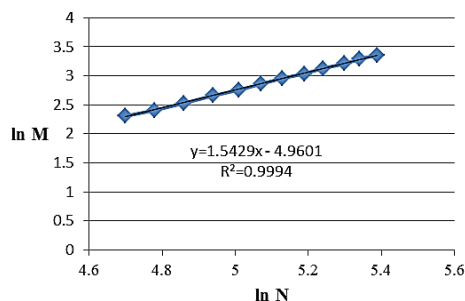


Fig. 3. A logarithmic plot of torque (M) vs rotational speed (rpm) (N) for sugarcane syrup at concentration of 72 °Brix and temperature of 65 °C.

By taking logarithm from both sides of the power-law equation (Ostwald de Waele) (Eq. 8), the following equation is obtained:

$$\text{Log } \sigma = \text{log } k + n \text{ log } \dot{\gamma} \quad (11)$$

Values of the consistency coefficient (k) and the flow behavior index (n) of sugarcane syrup are obtained from vertical intercept of logarithmic plot of shear stress versus shear rate.

From the results, it was found that in contrast to pekmez, all concentrations of sugarcane syrup are following the power-law, thickening with shear rate (Arslan et al., 2005; Yoğurtçu & Kamlı, 2005). For example, in studying rheological properties of the blend of tahin and pekmez, the flow behavior index (n) was reported in the range of 0.7-0.85 (Arslan et al., 2005).

Habibi Najafi and Alaei (2006) studied the rheological properties of different blends of date syrup (60 and 65 °Brix) and sesame paste (45, 50, and 55%). It was evident that these blends followed the power-law model. The values of consistency coefficient (k) ranged from 4.11 to 8.2 Pa sⁿ (> 1), and the flow behavior index (n) ranged between 0.34 and 0.7 (< 1) (Habibi Najafi & Alaei, 2006).

Fig. 4 shows the changes in consistency coefficient (k) and the flow behavior index (n) of sugarcane syrup by plotting the shear rate versus shear stress at a constant concentration (72 °Brix) and increasing temperature. The results of experiments showed that at three temperature levels (25, 45, 65 °C) and concentration of 72 °Brix, all three curves have non-Newtonian behavior following the power-law model (shear-thickening behavior).

The consistency coefficient (k), the flow behavior index (n), and the correlation coefficient of sugarcane syrup at temperature levels of 25, 45, and 65 °C and concentrations of 35, 55, and 72 °Brix are represented in Table 3 by the power-law. According to Table 3, the flow behavior index of all samples is greater than one ($n > 1$), so the sugarcane syrup is a non-Newtonian fluid that exhibits a power-law shear-thickening (Dilatant) behavior.

3.2.2. The effect of temperature on consistency coefficient

The consistency coefficient of syrup is a function of intermolecular forces that cause a restriction effect on molecular motion. These forces are affected by the variation in temperature. As the temperature increase, the intermolecular forces decrease, and consequently the consistency coefficient decreases (Mohammadzadeh Milani et al., 2019). Arrhenius equation (Eq. 9) was used to determine the effect of temperature on the consistency coefficient, and linear regression (Fig. 5) was used to determine the pre-exponential coefficient (K_{0T}) and activation energy (E_a) (Table 4). The activation energy shows the temperature dependence of the reaction (Mohammadzadeh Milani et al., 2019). By increasing the concentration of sugarcane syrup, the activation energy was increased as also reported by Yosefzadeh Sani et al. (2018) in watermelon juice, Mohammadzadeh Milani et al. (2019) in grape molasses, and Deshmukh et al. (2015) for clarified sapota juice.

Habibi Najafi and Alaei (2006) reported the value of activation energy for the blends of date syrup and sesame paste in the range of 22366-29478 KJ/mol, representing an ascending trend (Habibi Najafi & Alaei, 2006). In studying the rheological properties of a new dairy drink from milk and date extract concentrate (Dibbs) by Alhmadan (2002), the value of activation energy by the Arrhenius equation was reported between 5×10^3 to 21×10^3 KJ/kg mol at shear rate of 100 s^{-1} (Alhmadan, 2002).

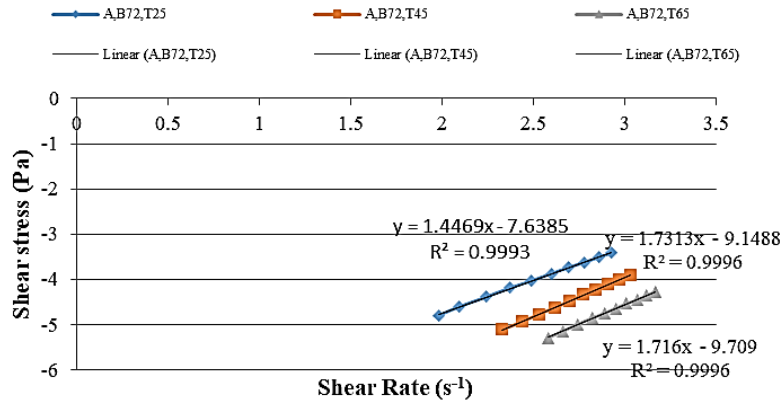


Fig. 4. Shear stress (Pa)-shear rate (s^{-1}) behavior of sugarcane syrup at concentration of 72 °Brix and different temperatures.

Table 3. The consistency coefficient, flow behavior index and correlation coefficient of sugar cane syrup (power-law model).

Model	°Brix	Temperatures (°C)								
		25			45			65		
		k (Pa S ⁿ)	R ²	n	k (Pa S ⁿ)	R ²	n	k (Pa S ⁿ)	R ²	n
Power-law	35	159532.03	0.995	1.759	194852.86	0.997	1.648	95798.27	0.992	1.738
	55	21036.19	0.996	1.443	22004.45	0.997	1.508	19574.83	0.999	1.516
	72	2075.58	0.999	1.716	16465.12	0.999	1.731	9395.63	0.999	1.446

Zuritz et al. (2005) studied the rheological behavior of grape juice and concentrated grape juice from the Mendoza region in Argentina. The studies were conducted on clear grape juice and concentrated grape juice at concentrations of 22.9-70.6 °Brix and temperatures of 20-80 °C. According to the results, the juices exhibited a Newtonian flow behavior. The effect of temperature on viscosity was well correlated with the Arrhenius equation. The effect of soluble solids concentration on activation energy was also studied, and it was found that an increase of solids concentration was concomitant with the increase in activation energy from 16.3 to 52.0 KJ/mol (Zuritz et al., 2005).

Table 4. Activation energy and pre-exponential coefficient of sugarcane syrup at different concentrations.

Brix	K _{0T} (Pa S ⁿ)	E _a (KJ /mol)	R ²
35	1.89 × 10 ⁻⁷	23695.75	0.997
55	7.71 × 10 ⁻⁹	36375.06	0.982
72	5.12 × 10 ⁻⁹	42402.93	0.994

Table 5. Parameters of exponential model at different temperatures.

Temperature (°C)	K _{0C}	B	R ²
25	6.32 × 10 ⁻⁵	0.1	0.992
45	4.27 × 10 ⁻⁵	0.094	0.995
65	4.63 × 10 ⁻⁵	0.076	0.973

3.2.3. The effect of concentration on consistency coefficient

An exponential equation (Eq. 10) was used to determine the effect of concentration (°Brix) on the consistency coefficient (*k*) of sugarcane syrup. By taking the logarithm of both sides of the equation and using linear regression (Fig. 6), the parameter of K_{0C} and B were calculated (Table 5). Considering the exponential model for evaluating the effect of concentration on consistency coefficient is also suggested by Mohammadzadeh Milani et al. (2019), Özkal and Süren (2017), Deshmukh et al. (2015), and Arslan et al. (2005) for grape molasses, poppy seed paste/grape pekmez blends, clarified sapota juice, and pekmez and tahin blend, respectively. The exponential model is reported as the preferred model for studying the effect of concentration on the rheological parameters in concentrated fruit juices, and the power-law model is usually used for puree foods (Mohammadzadeh Milani et al., 2019).

Kaya and Belibagli (2002) investigated the rheological properties of solid pekmez (°Brix= 82.1) at four different solid contents (52.1, 57.2, 66.8, and 72.9 °Brix) and five different temperature levels (50, 40, 30, 20, and 10 °C) by a controlled stress rheometer. They found that solid pekmez had non-Newtonian behavior, while diluted samples had Newtonian behavior. They also showed the effect of soluble solids concentration on viscosity using an exponential equation (Kaya & Belibagli, 2002).

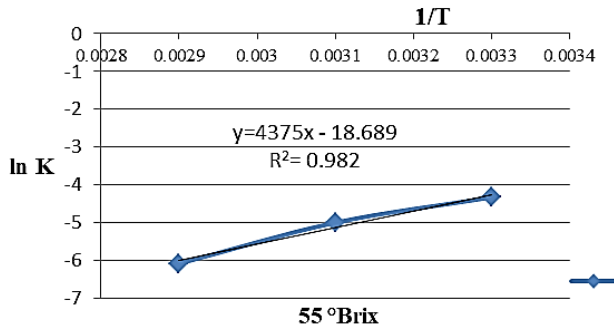


Fig. 5. A logarithmic plot of consistency coefficient according to $1/T$.

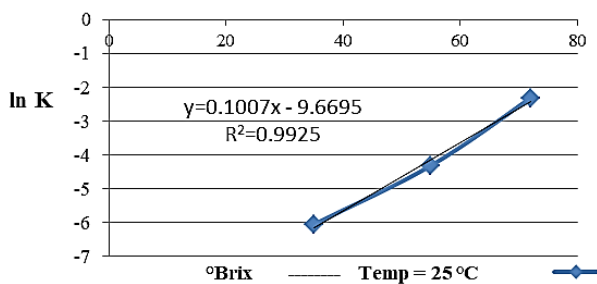


Fig. 6. Effect of concentration on consistency coefficient of sugarcane syrup by exponential model.

4. Conclusion

The sugarcane syrup, evaluated at three temperature levels (25, 45, and 65 °C) and concentrations of 35, 55, and 72 °Brix, is found to behave as a non-Newtonian fluid that exhibits power-law shear-thickening (Dilatant) behavior. The results showed that changes in concentration and temperature affected the sugarcane syrup viscosity. The temperature dependence of viscosity was evaluated by the Arrhenius equation, and it was found that the viscosity decreased as the temperature increased ($R^2 = 0.9925$). The activation energy of sugarcane syrup ranged from 23695 to 42402 KJ/mol, and by increasing concentration (°Brix), the activation energy also increased. Comparing the relative goodness of fit of the experimental rheological data of sugarcane syrup to other rheological models is suggested.

Acknowledgment

Not applicable.

Conflict of interest

The authors declare that they have no conflict of interest.

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