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SODIUM SESQUICARBONATE (AKANG) AND LIMESTONE AS CATALYSTS FOR THE SYNTHESIS OF MONOGLYCERIDES BY GLYCEROLYSIS OF PALM AND PALM KERNEL OILS

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ABSTRACT

Production of monoglycerides from palm and palm kernel oils were carried out using sodium sesquicarbonate (akang) and lime stone as catalysts.The results showed that the maximum monoglyceride formed is in the range of 49–57% of the fatty product for the limestone catalyst and 78 – 92% for the sodium sesquicarbonate catalyst at equilibrium stage of the reaction. The limestone catalyst substantially increases the initial rate of reaction without appreciably lowering the time required for attaining the equilibrium concentration of monoglyceride in the resulting reaction mixture compared to the sodium sesquicarbonate catalyst. Viscosity results showed that sodium sesquicarbonate increases the viscosity of the oils based – monoglycerides while limestone was found to decrease the viscosity rather. Solubility test showed that both monoglycerides were soluble in polar solvents and insoluble in the non polar solvent.

KEYWORDS: Sodium sesquicarbonate, limestone, monoglyceride, viscosity

INTORDUCTION

Sodium sesquicarbonate ($Na_2CO_3.NaHCO_3.2H_2O$) locally known as akang (Efik), kaun (Yoruba), kanwu (Hausa), akanwu (Igbo), and bettieh (Bette in Obudu) is systematically called trisodiumhydrogencarbonate [$Na_3H(CO_3)_2.2H_2O$] which is a double salt of sodium bicarbonate and sodium carbonate. The term is also applied to an equimolar mixture of those two salts with water of hydration (Mathew, 2005). Sodiunsesquicarbonate is used in place of the alkaline filtrate of the ash in local soap making, as food additive in meals preparation and other areas of life (Morah, 1999). To some extent, the monohydrate process is used to extract sodium sesquicarbonate from trona and this involves crushing and screening of the bulk trona ore which principally contains 90 – 95% sodium sesquicarbonate (Snelling, 2002). The crushed and screened trona is then calcinated at elevated temperatures to covert the ore sodium bicarbonate to crude sodium sesquicarbonate (Snelling, 2002). Limestone is produced from the mineral calcite ($CaCO_3$) and sediments. The main source of limestone is the limy formed in the ocean. According to Scholz (1995), limestone is a very common sedimentary rock of biochemical origin. The color variation in limestone is almost due to its iron content and some of the darkest colours may be due to carbon or possibly manganese (Berz, 1997).

This work is aim at investigating the catalytic activity of two locally found and readily available catalysts; sodium sesquicarbonate and limestone the synthesis of monoglycerides by glycolysis of palm and palm kernel oils.

Experimental procedures

1.1 Preparation of Palm and Palm kernel OilsMonoglycerides using Sodium sesquicarbonate (Akang)

Varied amounts of sodium sesquicarbonate (0.01g, 0.02g, 0.03g, 0.04g and 0.05g) were powdered and added to 156g of palm oil and the mixture thoroughly stirred in a 500 mL beaker. The substance obtained was then dissolved in 184g of glycerol and the mixture heated using a Bunsen burner at 240 – 248^{0}C for about 3 hours.A homogeneous mixture was obtained and the mixture was allowed to cool for over an hour. This homogeneous mixture was further dissolved in 50g diethyl ether and a two-phased separable mixture was obtained. It was then separated using a separating funnel and the monoglyceride collected, packed and stored. The same procedure was applied to the preparation of sodium sesquicarbonate/palm kernel based monoglyceride (SSPKOM).In other to avoid excessive wear of the homogenizer, sand and other insoluble impurities which may follow inferior grades of sodium sesquicarbonate was thoroughly separated. All measurements werecarried out accurately in both experiments involving both catalysts in order not to have varying percentages that may affect comparism and the temperature of the heat supplied was monitored closely to avoid over heating of the oils.

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1.2 Preparation of Palm and Palm kernel Oils Monoglycerides using Limestone

Varied amounts of limestone (0.01g, 0.02g, 0.03g, 0.04g and 0.05g) were powdered and added to 156g of palm oil and the mixture thoroughly stirred in a 500ml beaker. The substance obtained was then dissolved in 184g of glycerol and the mixture heated using a Bunsen burner at 240 – 248^{0}C for about 3 hours. A homogeneous mixture was obtained and the mixture was allowed to cool for over an hour. This homogeneous mixture was further dissolved in 50g diethyl ether and a two-phased separable mixture was obtained. It was then separated using a separating funnel and the monoglyceride collected, packed and stored. The same procedure was applied to the preparation of limestone/palm kernel based monoglyceride (LPKOM).

RESULTS AND DISCUSSION

2.1 Effect of catalysts on density of modified palm and palm kernel oils

Monoglycerides are intermediates in the degradation of diglycerides and triglycerides (Abraham *et al.,* 1984; Holmberg and Osterberg, 1988). In effect therefore, the weight of the monoglycerides should be lower than that of the diglycerides and triglycerides (unmodified oils) respectively. The results shown in Tables 1 – 4 indicate that weight of the modified oils was less than that of the unmodified oils while the density of the modifies oils was greater than that of the unmodified oils (palm and Plalm kernel oils) respectively.The shift in weight away from the weight of the unmodified oils shows that the modified oils are monoglycerides (Leila and Rogerio, 1998).

2.2 Viscosity analysis test

The viscosity test was carried out using the Ostwald Viscometer apparatus and the equation used is given below:

$$\cap_2 = \cap_1 \frac{d_2\, t_2}{d_1\, t_1} \qquad 1$$

where $\cap_2$ is the sample viscosity, d_1 the density of reference (water), t_2 the retention time of sample, t_1 the retention time for reference (water), d_2 is the sample density and $\cap_1$ is the viscosity of reference (Fregoleate*et al.*, 2006). Following the equation above, the following constants were used: d_1 = 0.998mg/cm^3, t_1 = 4 sec and $\cap_1$ = 1.19 x 10^{-3} poise for the reference fliud.

It was observed that the viscosity of sodium sesquicarbonate catalyzed palm and palm kernel oils - based monoglycerides continue to increase with increase catalyst concentration (Table 1 – 2). Figs. 1 – 2 also show that palm oil is a better oil than palm kernel oil in the preparation of monoglycerides and this can be attributed to the high percentage of fatty acids present in palm oil as compared to palm kernel oil (Basu 1962) and (Angela *et al*, 2008).The sudden increase in the viscosity of the monoglyceride is attributed to the pH of the catalyst (pH 13) which affects the variable composition of the oils (Ferretti*et al.*, 2011; Fregoleate*et al.*, 2010), unlike the viscosity of the limestone catalyzed palm and palm kernel oils - based monoglycerideswhich continue to decrease with increase catalyst concentration (Tables 3 – 4 and Fig. 2).It is also observed that the viscosities of the unmodified palm and palm kernel oils are far lower than those of the modified oils (monoglycerides).Sodium sesquicarbonate catalyst substantially increases the time required to reach the equilibrium concentration ofmonoglycerides in the reaction mixture. The limestone catalyst decreased this time as its concentration is increased, and this is as a result of its pH which is almost neutral and as a result making the sodium sesquicarbonate a better catalyst to limestone (Figs. 3 – 4) as confirmed by Martinez *et al.* (2005); Hernandez and Otero (2009); Lilia *et al* (2012).

Table 1: Calculated values of retention time, weight, density and viscosity of modified palm oil (Monoglyceride) using the sodium sesquicarbonate (*akang*)catalyst at 248^{0}C.

Mass of akang(g)	Retention time(sec)	weight of sample(g)	Density(g/cm3)	Viscosity (poise)
0.00	344.00	45.70	0.91	7945.80
0.01	802.80	10.30	1.03	16382.90
0.02	972.60	10.80	1.08	18929.10
0.03	1142.20	11.20	1.12	21436.00
0.04	1312.20	11.70	1.17	23574.00
0.05	1482.10	12.00	1.20	25960.70

Table 2: Calculatedvalues of retention time, weight, density and viscosity of modified palm kernel oil (Monoglyceride) using the sodium sesquicarbonate (*akang*)catalyst at 248^{0}C.

Mass of akang(g)	Retention time(sec)	weight of sample(g)	Density(g/cm3)	Viscosity (poise)
0.00	166.00	45.60	0.90	2709.20
0.01	583.20	11.50	1.15	10659.60
0.02	669.60	12.60	1.26	11170.30
0.03	811.20	13.19	1.32	12917.40
0.04	919.20	13.54	1.35	14311.90
0.05	1020.60	14.22	1.42	15107.30

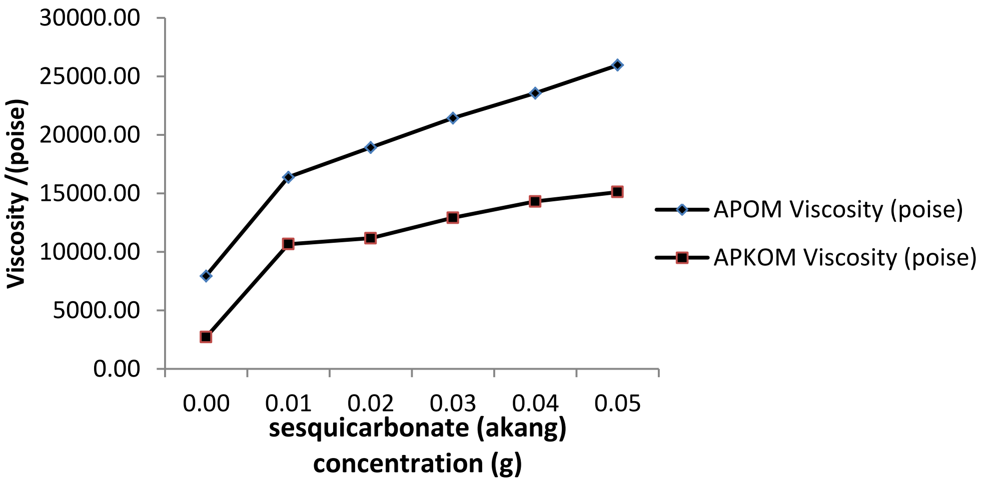

Fig. 1: Variation of viscosity (poise) with sodium sesquicarbonate (akang)concentration (g) in palm and palm kernel oils monoglycerides.

Table 3: Calculated values of retention time, weight, density and viscosity of modified palm oil (Monoglyceride) using the Limestone catalyst at 248^{0}C

Mass of akang(g)	Retention time(sec)	weight of sample(g)	Density(g/cm3)	LPOM Viscosity (poise)
0.00	344.00	45.70	0.91	7945.80
0.01	561.60	11.20	1.12	10537.80
0.02	565.80	11.70	1.17	10164.80
0.03	570.00	11.80	1.18	10153.40
0.04	574.20	12.29	1.22	9892.90
0.05	578.40	12.90	1.29	9424.50

Table 4: Calculated values of retention time, weight, density and viscosity of modified palm kernel oil (Monoglyceride) using the Limestone catalyst at 248^{0}C

Mass of akang(g)	Retention time(sec)	weight of sample(g)	Density(g/cm3)	LPKOM Viscosity (poise)
0.00	166.00	45.60	0.90	2709.20
0.01	546.00	11.30	1.13	9351.10
0.02	547.20	12.30	1.23	9351.10
0.03	547.80	12.40	1.24	9285.80
0.04	548.40	12.60	1.26	9148.40
0.05	549.90	12.70	1.27	9101.20

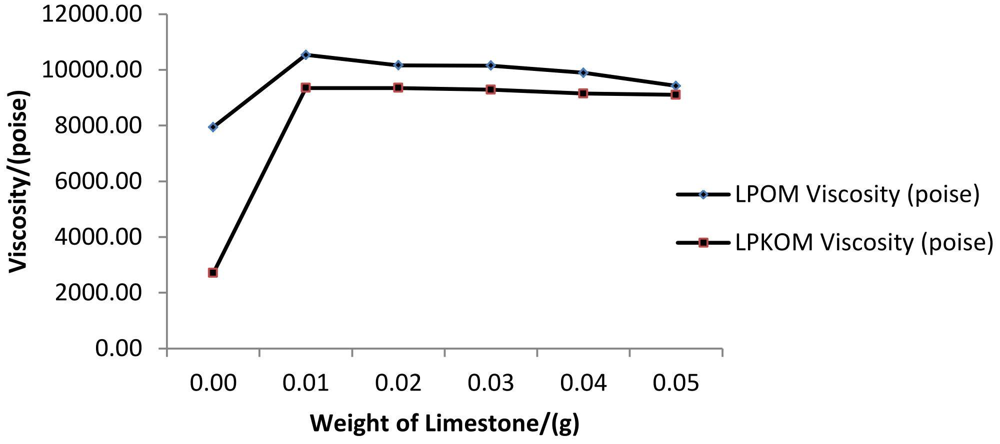

Fig. 2: Variation of viscosity (poise) with Limestone (catalyst) concentration (g) in palm and palm kernel oils monoglycerides.

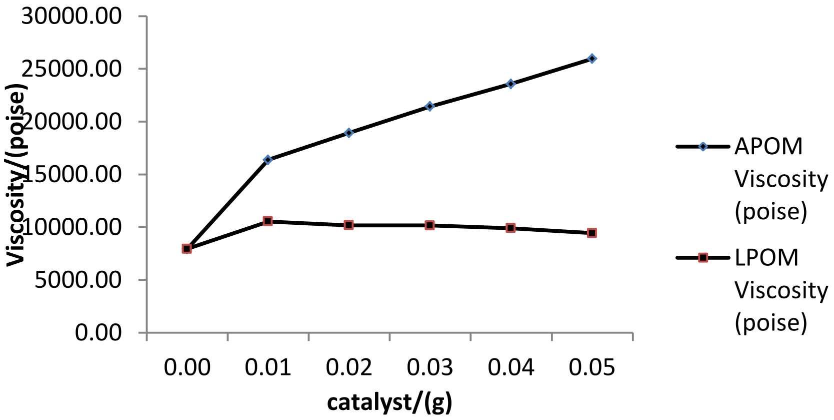

Fig. 3: Variation of viscosity (poise) with sodium sesquicarbonate (akang) and Limestone catalyst concentrations (g) in palm oilmonoglycerides.

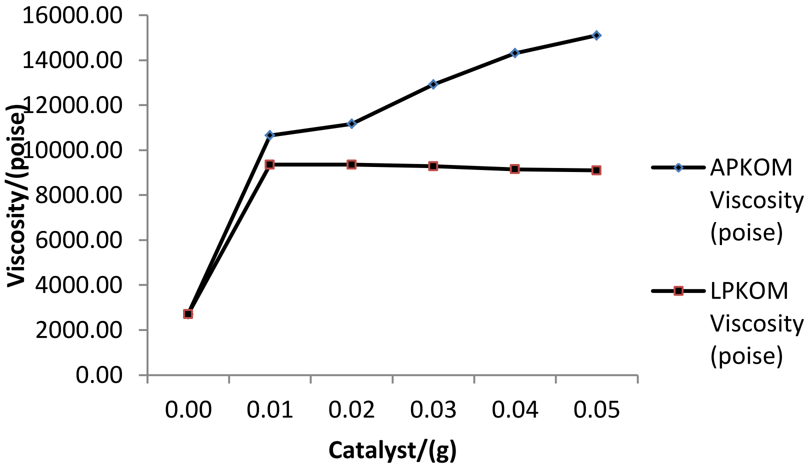

Fig. 4: Variation of viscosity (poise) with sodium sesquicarbonate (akang) and Limestone catalyst concentrations (g) in palm kernel oil monoglycerides

2.2 Solubility analysis test

To ascertain the true state of the monoglyceride prepared, a solubility test was carried out. Ethanol and water were used as the polar solvents while acetone and chloroform were used as the non polar solvents. Sodium sesquicarbonate catalyzed monoglyceride prepared from palm and palm kernel oils were absolutely soluble in polar solvents - water and ethanol and completely insoluble in the non polar solvents - Acetone and Chloroform (Tables 5 – 6). The same reaction was obtained from the limestone catalyzed monoglyceride prepared from palm and palm kernel oils (Tables 8 – 9). The solubility result obtained from both compounds and other characteristics exhibited by them show that they prepared mixtures are truly monoglycerides. Solubility of monoglycerides in polar solvents can be explained as a result of the hydrogen – oxygen bond which exist in both the monoglyceride and polar solvent (Casimir*et al.*, 1992; Guan-Chiun*et al.*, 2004; Abraham *et al.*, 1984). Also, this can be attributed to the absorption of energy by the solution process, amount of carbon branching which increases the solubility since more branching will reduce the size (or volume) of the molecule and make it easier to solvate the molecules with solvent and also dipole – dipole interaction between monoglyceride and solvent (Inger and Magnus, 1999; Alexsandra*et al*, 2009).Alexsandra*et al*. (2009) showed the behavior of some monoglycerides in the presence of polar and nonpolar solvents. It showed that 90% of different monoglycerides containing blends are soluble in polar solvents. Alexsandra*et al*. (2009) further explains that as water is added, the apparent melting point (m.p) drops, then the viscosity of the monoglyceride begins to decrease. The viscosity becomes so low as the percentage of the water keeps increasing. The polar solute molecules have a positive and negative end to the molecule. If the solvent molecule is also polar, then positive ends of solvent molecules will attract negative ends of solute molecules (Fregoleate*et al.*, 206 and 2010) and (Ferrette*et al.*, 2011).

Table 5: Variation in solubility of Sodium sesquicarbonate catalyzed palm oil monoglyceride polar and non polarin solvents.

Mass of Sodium Sesquicarbonate(g)	Polar solvent		Non polar solvent	
	Water	Ethanol	Acetone	Chloroform
0.01	+	+	-	-
0.02	+	+	-	-
0.03	+	+	-	-
0.04	+	+	-	-
0.05	+	+	-	-

Table 6: Variation in solubility of sodium sesquicarbonate catalyzed palm kernel oilmonoglyceride inpolar and non polarsolvents.

Mass of Sodium sesquicarbonate(g)	Polar solvent		Non polar solvent	
	water	ethanol	Acetone	chloroform
0.01	+	+	-	-
0.02	+	+	-	-
0.03	+	+	-	-
0.04	+	+	-	-
0.05	+	+	-	-

Table 7: Variation in solubility of Limestone catalyzed palm oil monoglyceride in polar and non polar solvents.

mass of Lime stone(g)	Polar solvent		Non polar solvent	
	water	ethanol	acetone	chloroform
0.01	+	+	-	-
0.02	+	+	-	-
0.03	+	+	-	-
0.04	+	+	-	-
0.05	+	+	-	-

Table 8: Variation in solubility of Limestone catalyzed palm Kernel oil monoglyceride in polar and non polar solvents.

Mass of Limestone(g)	Polar solvent		Non polar solvent	
	water	ethanol	acetone	chloroform
0.01	+	+	-	-
0.02	+	+	-	-
0.03	+	+	-	-
0.04	+	+	-	-
0.05	+	+	-	-

CONCLUSIONS

1. Sodium sesquicarbonate catalyst is a better catalyst than limestone.

2. Viscosities of Sodium sesquicarbonate catalyzed monoglycerides prepared from palm and palm kernel oils show increase from the viscosities of the unmodified oils as the concentration increases.

3. Viscosities of Limestone catalyzed monoglycerides prepared from palm and palm kernel oils show gradual fall towards the viscosities of the unmodified oils as the concentration increases.

4. Sodium sesquicarbonate and Limestone catalyzed monoglycerides prepared from palm and palm kernel oils are absolutely soluble in polar solvents - water and ethanol and completely insoluble in the non polar solvents - Acetone and Chloroform.

5. Weight of the modified oils was less than that of the unmodified oils while the density of the modified oils was greater than that of the unmodified oils (palm and Plalm kernel oils) respectively. The high level of shift in weight away from that of the unmodified oils shows that the modified oils are monoglycerides

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