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COAST
JOURNAL OF THE SCHOOL OF SCIENCE
Volume 6, Issue 1. May, 2024 ISSN: 2714-3716
Coast, J. Sch. Sci. 6 (1): 946- 953

THERMAL STABILITY STUDY OF METAL CARBOXYLATES OF *Cucurbita pepo* SEED OIL

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https://doi.org/10.61281/coastjss.v6i1.1

Abstract

The study investigated the thermal stability of *Cucurbita pepo* seed oil carboxylates in the temperature range of 433, 453 and 473K. The carboxylates, prepared via metathesis in ethanol, exhibited characteristic vibrations (1633-1398 cm^{-1}) confirming formation of the carboxylates. The decomposition rate constants were found to be of the order of 10^{-3} min^{-1}, with activation energy values spanning 12.0-18.4 kJ mol^{-1}. The activation enthalpy ($\Delta H^{\ddagger}$) was observed in the range of 8.03-14.47 kJ mol^{-1}, indicating an endothermic behavior. The non-spontaneous decomposition process, indicated by $\Delta G^{\ddagger}$ (113.7-115.7 kJ mol^{-1}) and $-\Delta S^{\ddagger}$ (0.227-0.244 kJ mol^{-1} K^{-1}), identified Ba-PSO as the most stable. This suggests the potential use of *Cucurbita pepo* seed oil for metal carboxylate synthesis thereby, enhancing its commercial value and promoting its cultivation in Nigeria.

Key words: Thermal stability, metal carboxylates, kinetics parameters, infrared spectra

Introduction

Seed oils are derived from the endosperm of plant seeds rather than the pericarp of fruits, which play a crucial role in various sectors, owing to their nutritional, industrial, and medicinal attributes (Oderinde *et al.,* 2009). Diverse seed oils, such as sunflower, pumpkin, corn, and sesame, find application in different industries. Notably, pumpkin (*Cucurbita spp.*) oil stands out for its distinctive functional properties, primarily attributed to its nutrient-rich composition, dominated by oleic and linoleic acids (Xiang *et al.,* 2017).

However, the quality of pumpkin seed oil is subject to influences such as temperature, soil type, growing conditions, and extraction techniques. A fascinating avenue emerging from the exploration of seed oils is the utilization of metal carboxylates, or metal soaps. These metal soaps, specifically alkaline-earth or heavy-metal long-chain carboxylates, are soluble in non-aqueous solvents but insoluble in water (Barth, 1982). Notable heavy metal soaps, including calcium, zinc, lead, cadmium, and barium, play essential roles as poly(vinyl chloride) heat stabilizers (Owen and Msayib, 1989; Bacaloglu and Fisch, 1994). Additionally, certain metal soaps facilitate paint drying in non-polar environments, while others inhibit corrosion.

Silver carboxylates contribute to thermographic and photothermographic materials, with copper soaps exhibiting fungicidal properties (Binnemans *et al.,* 2004). Pumpkin seed oil has emerged as a valuable resource, making significant contributions to industrial innovation in sectors like greases, cosmetics, and textiles (Egbuchunam *et al.*, 2005). The high oil content of pumpkin seed oil (ranging from 30 to 51%), primarily consisting of linoleic and oleic acids (27 to 38%), positions it as a promising candidate for the production of metal carboxylates.

Remarkably, beyond its industrial applications, pumpkin seed oil demonstrates therapeutic potential. Studies suggest its efficacy in inhibiting prostate cell growth, delaying hypertension progression, alleviating arthritis and high cholesterol, and impeding the growth of specific cancer cells. Despite these promising attributes, Nigeria's *Cucurbita pepo* oil faces commercial challenges due to the limited volume suitable for sale. Notably, scant research has delved into the synthesis of metal carboxylates, such as calcium, zinc, or barium, using pumpkin seed oil. This study aims to address this gap by creating and evaluating calcium, zinc, and barium carboxylates from *Cucurbita pepo* seed oil, with a focus on their thermal stability.

Materials and Methods

Sample collection and pre-treatment

The fruits of the plant were procured in Okitipupa, Ondo State and identified at the Biological Sciences Department (Botany Programme) of the University. The fruits were opened by knife and the seeds were collected. The seeds were air dried in the laboratory, deshelled, grounded with mortar and pestle. The oil was extracted with n-hexane using soxhlet apparatus,

Preparation of metal carboxylates

Metal soaps of *Cucurbita pepo* seed oil (PSO) were prepared via metathesis in ethanol solution following the method described by Burrows *et al.,* (1981). Approximately 9.2 g of the oil was dissolved in 50 ml of hot ethanol and treated with 20 ml of 20% (w/v) NaOH solution. A few drops of dilute HNO_3 were added to neutralize excess NaOH. Subsequently, 100 ml of 30% (w/v) of the corresponding metal salt was slowly added to the mixture with continuous stirring. The resulting metal carboxylates precipitated, washed with warm water, air-dried, and further dried in an oven at 60°C until a constant weight was achieved, following the method described by Folarin and Enikanoselu in 2010. For the preparation, analytical grade of the corresponding salts were used.

The FTIR spectra of both the oil and metal carboxylates were recorded using an Agilent FTIR-8400S at a scan rate of 4 cm^{-1} within the wave number range of 4000-650 cm^{-1}.

Thermal stability studies of the metal carboxylates

The thermal decomposition of metal soaps within the temperature range of 160 – 200°C was assessed through gravimetric measurements over time, following the protocol outlined by Egbuchunam *et al.* in 2005. Typically, 0.5g of the metal soap was precisely weighed into a pre-weighed tube and subjected to heating in a muffle furnace at the specified temperature for a defined duration (30 – 120 minutes). After completion of the heating period, the sample was removed from the furnace and allowed to cool in a desiccator. The final weight of the sample was measured, and the weight loss was determined using the expression:

$$\%\text{weight loss} = \frac{W_0 - W_t}{W_0} X\ 100$$

Where w_o is the initial weight of the metal carboxylate and wt is the residual weight of metal carboxylate after heating time (t).

Results and Discussion

The FTIR spectrum of the seed oil is shown in Figure 1. An ester or free acid v(C=O) in the seed oil is probably linked to the prominent band in the spectrum at 1744 cm^{-1}. The band in the 1370–1000 cm^{-1} range is attributed to the triglyceride v(C–O) in the oil. At 2922 and 2851 cm^{-1}, respectively, strong asymmetric and symmetric stretching vibrations of CH_2 were observed. The v(O-H) of free acid in the oil is responsible for the weak yet medium band at 3004 cm^{-1}. In the metal carboxylates spectra, all other bands disappear save for the 2922 and 2851 cm^{-1} bands. The carboxylate group exhibits asymmetric and symmetric stretching vibrations at 1650–1550 cm^{-3} and 1420–1300 cm^{-3}, corresponding to strong bands rather than a carbonyl band. The unique carboxylate vibrations—two asymmetric and one symmetric—indicates a bridging bidentate. Ba-PSO exhibits symmetric vibrations at 1405 cm^{-3} and asymmetric vibrations at 1572 and 1539 cm^{-3}. In Ca-PSO, symmetric vibrations are seen at 1461 cm^{-3} and asymmetric vibrations at 1572 and 1535 cm^{-3}. Asymmetric vibrations are seen in Zn-PSO between 1591 and 1535 cm^{-3}, while symmetric vibrations are observed at 1453 cm^{-3}. A monodentate coordination mode is suggested by the range of Δv values (difference between asymmetric and symmetric carboxylate stretching vibrations) of 111 to 167 cm^{-1}. The carboxylates' alkyl group's CH_2 stretching vibrations match the oil's spectrum. Wide bands in the region of 3004–2914 cm^{-1} could represent hydrogen-bonded OH groups, possibly originating from water. The synthesis of metal carboxylates has been validated by repeated observations (Folarin *et al.,* 2013, Folarin *et al.,* 2016).

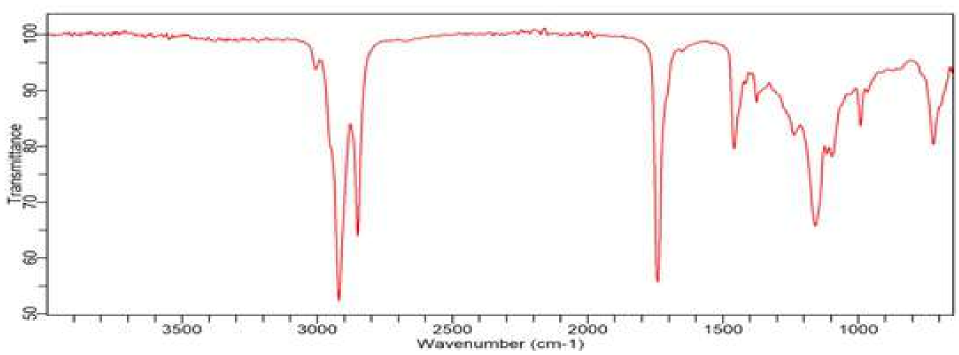

Figure1: FTIR spectrum of Pumpkin seed oil

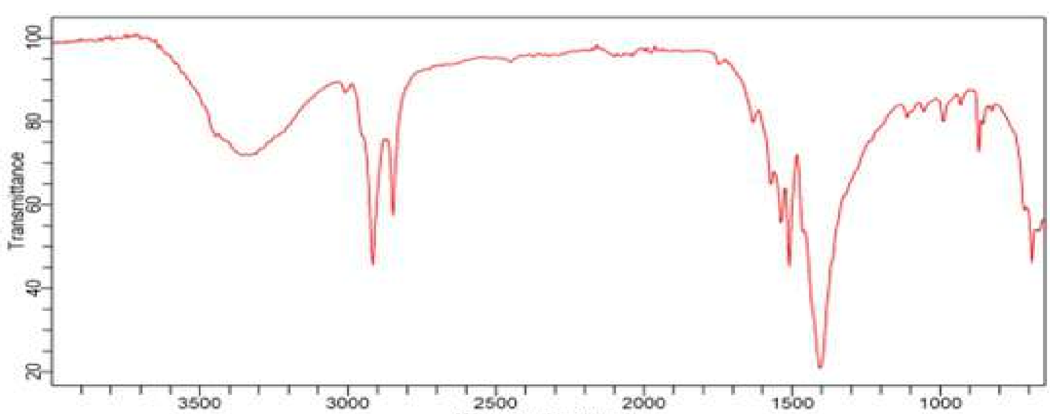

Figure 2: FTIR spectrum of Ba-PSO

Table 1: FTIR bands for *Cucurbita pepo* seed oil and the metal carboxylates

Assignment	PSO	Ba-PSO	Ca-PSO	Ca-PSO
O-H stretch cm^{-1}	3004	3008	2914	2918
CH_2, C-H Asymmetric Stretch cm^{-1}	2922	2914	2847	2847
CH_2, C-H Symmetric Stretch cm^{-1}	2851	2847	2847	2847
C=O stretch cm^{-1}	1744	1748	1736	1736
COO -Asymmetric Stretch cm^{-1}	-	1572,1539	1572, 1535	1591, 1535
C=O stretch cm^{-1}	-	1405	1461	1453
C-O stretch + O -H in plane deform cm^{-1}	1464	-	-	-
C-O stretch cm^{-1}	1237			
OH out of plane Deform cm^{-1}	-	827	872	728
CH_2 rocking cm^{-1}	723	689	711	719

Figures 3 - 5 show the decomposition at various time intervals of *Cucurbita pepo* seed oil metal soaps at 433, 453, and 473K. The findings demonstrated that, for the different temperatures at 433, 453, and 473K, the percentage weight losses of the carboxylates obviously increase with time. Metal oxides and carboxylic acids are produced during the multi-stage decomposition of metal carboxylates. (Binnemans *et al.*, 2004; Srinivasan and Sawant, 2003). The length of the carboxylic acids' alkyl chain determines how many and what kind of phase transitions occur. The weight loss that is observed during thermal decomposition is explained by the creation of gaseous and vapourizable chemicals. Based on the provided numbers, it can be inferred that barium soap has the lowest rate of decomposition among the metal soaps, making it the most thermally stable, whereas calcium soap has the highest rate of decomposition.

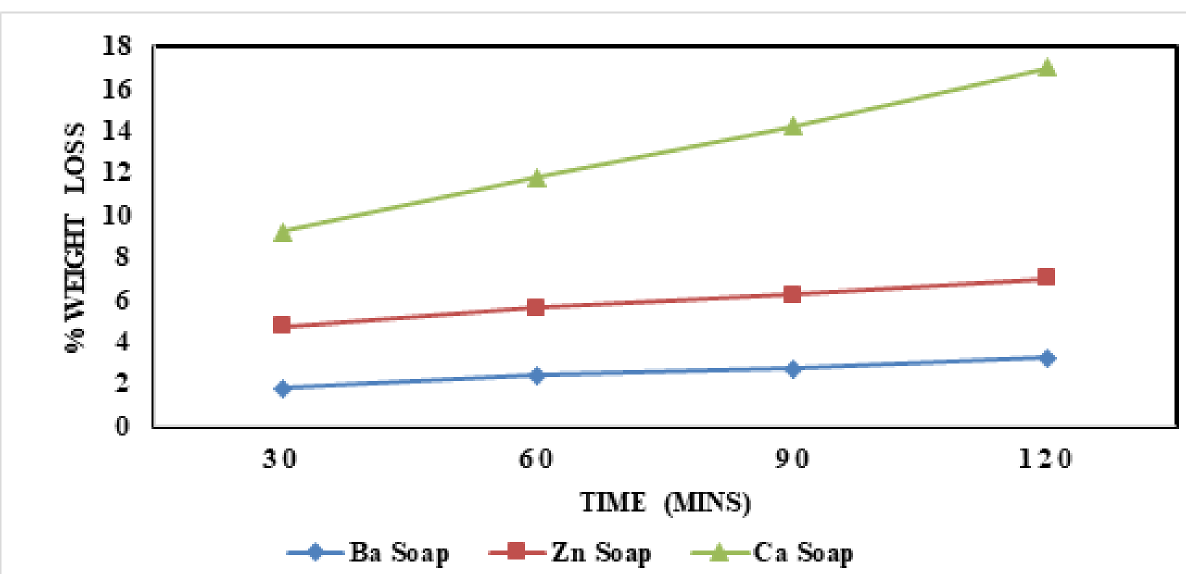

Figure 3: Decomposition of metal soaps of *Cucurbita pepo* seed oil at 433K

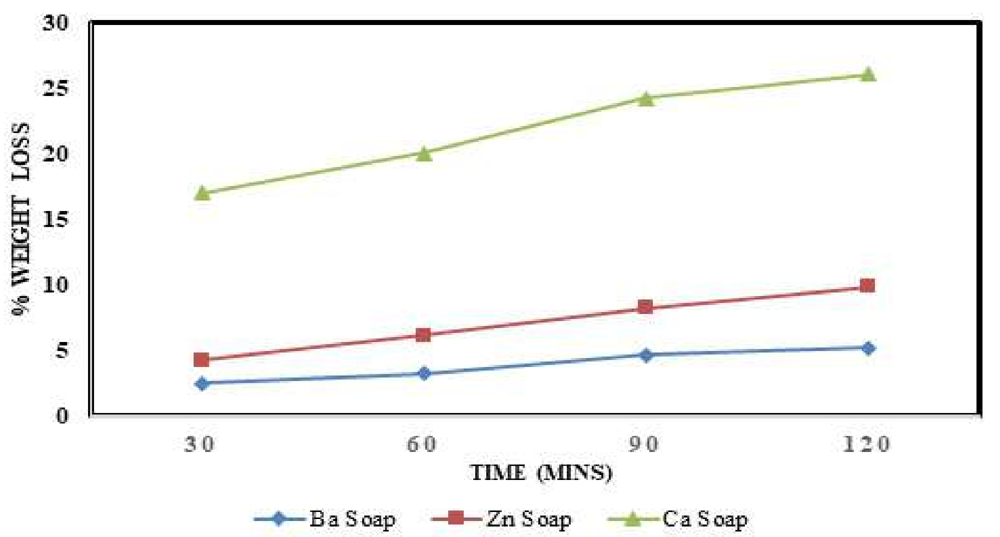

Figure 4: Decomposition of metal soaps of *Cucurbita pepo* seed oil at 453K

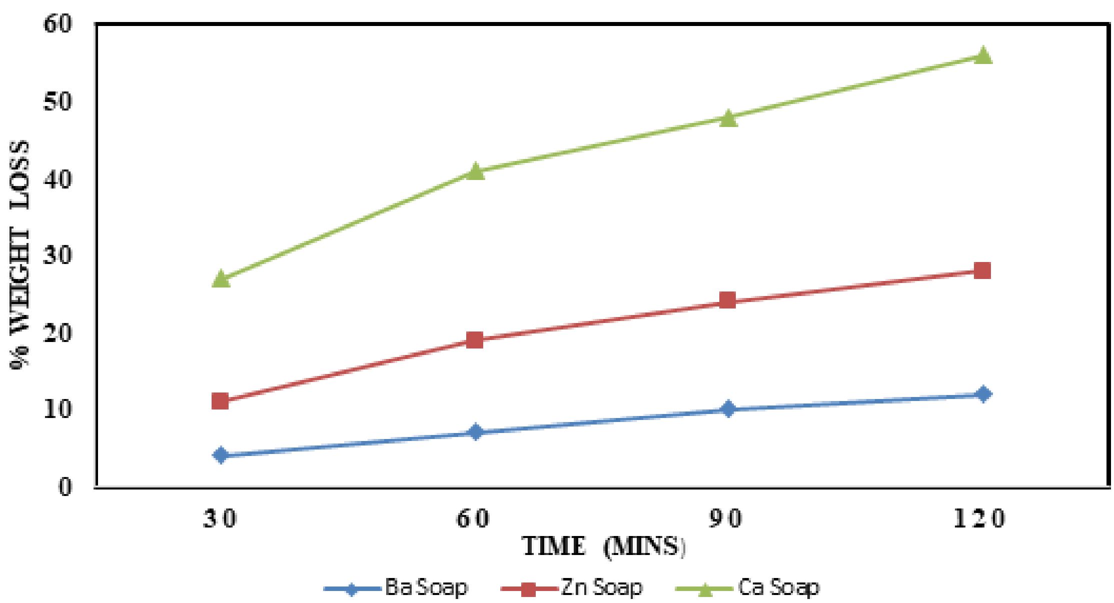

Figure 5: Decomposition of metal soaps of *Cucurbita pepo* seed oil at 473K

Table 2: Percentage (%) weight loss at 433K

Heating Time (mins)	%weight loss		
	Ba Soap	Zn Soap	Ca Soap
30	1.8	2.9	4.5
60	2.4	3.2	6.2
90	2.7	3.5	8.0
120	3.2	3.8	10

Table 3: Percentage (%) weight loss at 453K

Heating Time (mins)	%weight loss		
	Ba Soap	Zn Soap	Ca Soap
30	2.5	4.2	17
60	3.2	6.1	20
90	4.6	8.2	24
120	5.2	9.8	26

Table 4: Percentage (%) weight loss at 473K

Heating time (mins)	%weight loss		
	Ba Soap	Zn Soap	Ca Soap
30	4	7	16
60	7	12	22
90	10	14	24
120	12	16	28

The rate of thermal decomposition of metal soaps is generally considered to follow a first-order kinetics (Eghuchunam *et al.*, 2005; Okieimen *et al.*, 2006) and may be expressed as follows:

$$\frac{dw}{dt} = k\,(W_0 - W_t) \qquad (1)$$

Where W_0 is the initial weight of the metal soap andW_1 is the residual weight of the metal soap after heating while k is the rate constant. Rearranging and integrating (eqn 1) gave eqn 2.

$$\log (w_o - w_1) = \log w_o - \frac{kt}{2.303} \qquad (2)$$

The values of the rate constant for the decomposition of the metal soaps were obtained from the plots of the logarithm of %weight loss against time and the results presented in Table 2- 4.

Table 5: Rate constants for the decomposition of metal carboxylates of *Cucurbita pepo* seed oil

Metal carboxylate	Temperature(K)	Rate constant ($k\times10^{-2}$ min^{-1})
Ba-PSO	433	1.51
	453	1.64
	473	2.00
Ca-PSO	433	1.74
	453	2.10
	473	2.60
Zn-PSO	433	1.53
	453	1.84
	473	2.30

For Ba soap, Ca soap, and Zn soap, the rate constants are of the order $10^{-2}min^{-1}$ and are also temperature-dependent, increasing by 32.5%, 49.4%, and 50.3%, respectively, within the temperature range. The energy barrier that a reaction must cross is measured by its rate constant; the lower the barrier, the higher the rate constant (Bruice, 1998). Values for the activation energy (Ea) of the decomposition of the metal soaps were determined from the dependence of the rate constant values on temperature. This relationship and the result are shown in Table 5.

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2+T_1}{T_2T_1}\right) \tag{3}$$

The metal soaps have an activation energy that ranges from 12.0 to 18.4 $kJmol^{-1}$ when they break down. The lowest value is 12.0 $kJmol^{-1}$ for zinc soap, the maximum value is 18.4 $kJmol^{-1}$ for barium soap, and the value of 16.2 $kJmol^{-1}$ is for calcium soap. These results are in line with those documented for rubber seed oil metal soaps (Okieimen *et al.,* 2006). Using the formula $\Delta H^{\neq} = Ea - RT$, the values of the enthalpy of activation, $\Delta H^{\neq}$, for the decomposition of the metal carboxylates were computed, with the results displayed in Table 6. The process is endothermic, based on the values of the enthalpy of activation.

Table 6: Thermodynamic parameters for the decomposition of metal carboxylates of *Cucurbita pepo* seed oil

Metal carboxylate	E_a ($kJmol^{-1}$)	$\Delta H^{\neq}$ ($kJmol^{-1}$)	$\Delta G^{\neq}$($kJ\ mol^{-1}$)	$-\Delta S^{\neq}$ ($kJ\ mol^{-1}\ K^{-1}$)
Ba-PSO	18.4	14.47	115.7	0.244
Ca-PSO	16.2	12.26	113.7	0.239
Zn-PSO	12.0	8.03	112.9	0.227

The true energy barrier to a reaction is given by the free energy of activation, $\Delta G^{\neq}$, (Bruice, 1998), and this was determined using the expression: $\Delta G^{\neq} = -RT\,(2.303\log kh/Tk_B)$. The decomposition of metal soaps can be attributed to changes in entropy or enthalpy, although most reactions are driven by a combination of entropy and enthalpy (Bruice, 1998). The activation entropy, $\Delta S^{\neq}$, was computed as follows: $\Delta S^{\neq} = (\Delta H^{\neq} - \Delta G^{\neq})/T$. Table 6 also displays the findings of the activation entropy and free energy for the breakdown of the metal soaps. The results of the free energy of activation indicated that Ba soap is the most stable metal soap and Ca soap is the least stable, and the values obtained for $\Delta G^{\neq}$ and $\Delta S^{\neq}$ demonstrate that the decomposition of the metal soaps is a non-spontaneous process.

Conclusion: In this study, thermal stability of metal soaps of *Cucurbita pepo* seed oil prepared by metathesis in ethanol was assessed. Barium soap is the most stable while zinc soap is the least stable based on the kinetics parameters. The formation of the metal soaps was confirmed by FTIR spectroscopy. The kinetics parameters of the metal soaps show potential of the oil for the preparation of metal carboxylates. This study points towards promising industrial applications and utilization of the oil and promotes its cultivation in Nigeria.

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