



Influence of Extraction Temperature on the Quality of Neem Seed Oil: Preliminary Investigation

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Abstract: The storage of neem oil for a long time before usage comes along with challenge of quality retain ability of the oil; and the extraction methods can affect the quality of neem seed oil. This research work compared the mechanical expression method to the solvent extraction method to find a better method that will give high-grade neem oil for long-term storage. A plant with a capacity of 50 kg/day of neem seed kernel was used to extract oil from neem seed using ethanol as extraction solvent. The increase of extraction temperature from 20 °C (mechanically expressed) to 78 °C leads to decrease of iodine value from 62.70 to 60.10 gI₂/100 g; increase of acid value from 3.4 to 4.2 mg KOH/g and increase of saponification value from 158.74 to 210.18 mgKOH/g. The Fames standard method was used for the GC – MS analysis and the percentage composition of the polyunsaturated components in the 20 °C (mechanically expressed), 50 °C, 55 °C, 60 °C and 78 °C oils were 21.58, 6.33, 3.09, 1.83 and 0.21% respectively. The changed of extraction temperature from 20 °C to 78 °C brings about reduction of polyunsaturated components from 21.58% to 0.21%. The increase of extraction temperature leads to conversion of unsaturated components to saturated components due to auto – oxidation process. This is clearly seen as the extraction temperature increased from 20 °C to 78 °C, the percentage composition of the saturated components increased from 22.40% to 43.70% and the polyunsaturated component decreased from 20.47% to 0%. The fatty acid composition associated with the 78 °C oil are: Oleic acid, 46.61%; Stearic acid, 11.83%; Palmitic acid, 16.54%; 11 – Octadecenoic acid, 3.58%; Cis – Vaccenic acid, 5.90%; Cyclopropaneoctanal, 11.19%; Squalene, 0.21% and Trimethylsilyl – di(trimethylsiloxy) – silane, 4.14%. The functional groups identified in the 78 °C oil were C – H, C = O, C – C and C – O. Based on the lowest iodine value, lowest percentage composition of the polyunsaturated component value and high percentage composition of saturated component, the neem oil obtained at 78 °C from the miscella is considered as the high grade neem oil because it is less reactive due to lowest percentage composition of polyunsaturated and can be stored for long time before usage. Furthermore, the results from this work will assist manufacturers in selecting the extraction temperature for particular application of the neem seed oil. The extracted oil is recommended for soap production due to its high saponification value.

Keywords: Neem Tree, Acid Value, Iodine Value, Saponification Value, Auto-oxidation.

1. INTRODUCTION

Neem tree is highly medicinal and cultivated in different part of the world such as Asia (India and Indonesia), Africa, America and Europe [1,2]. Over four million (> 4 000 000) neem trees are in Borno, Kano, Katsina and Sokoto in Nigeria; and 90% of the Savanna Zone forestry of Nigeria is covered by Neem tree under the afforestation programme [3]. The vegetable oil such as neem oil is greatly use in cosmetic, soap and agricultural industries and in the production of pharmaceutical drugs [4]. Ethanol is highly recommended for oil extraction because it is safe, environmentally friendly and is a green (renewable) solvent [4, 5]. The quality of neem oil is of commercial and industrial value as it determines its suitability for biodiesel, cosmetics and soap production and equally for pharmaceutical application. The quality is expressed in terms of iodine, acid and saponification values. Extraction parameters such as contact time, particle size, solid – solvent ratio, solvent type, extraction temperature and medium agitation have effect on the yield of oil, but extraction temperature has additional effect on the quality of extracted neem oil [6, 7]. Acid value indicates the level of free fatty acid in the oil. Iodine value is a measure of the level of unsaturation of the oil and it indicates the long-term stability properties of the oil, a factor to consider in storage of the oil. The saponification value is an indicative of the presence of lower molecular components / short chain fatty acids in the oil.

To boost the production of high – grade neem oil that will retain its quality after storage before usage for industrial application such as soap and cosmetics production, the iodine value (65 – 80 g/g) characterized by good storage stability must be minimize. The high – grade neem oil in term of low iodine value is achievable when solvent extraction method is implored at higher extraction temperature than the mechanical expression which occurred at atmospheric temperature. The

result of this work will assist manufacturers in selecting the extraction temperature for particular application of the neem seed oil based on the oil needed quality.

The oil is mainly made of up triglyceride, which is a molecule of glycerol and three molecules of fatty acid [5]. The triglyceride can either be saturated, monounsaturated or polyunsaturated. The saturated compound has single bond (C – C) between the carbon atoms and is saturated with hydrogen atoms. The unsaturated compound has double bonds (C = C) between the carbon atoms [8, 9]. The neem oil has a shelf life up to eight months without any change under room conditions [4]. The best method of preserving neem oil is in the refrigerator or at room temperature inside a brown bottle [10]. Neem oil quality is affected by temperature, hydrolysis, oxidation, lipase enzyme and other compound found in the oil. Vegetable oil (Neem oil) contain lipase enzyme which has an optimum temperature of about 35 - 40°C. The lipase enzyme normally hydrolyzes oil to form free fatty acid and glycerol [11]. The stability of the neem oil is its ability to retain its properties such as physical, chemical and microbiological within a specified limit throughout the shelf – life [10]. Care must be taken to preserve the quality of the oil during storage. If not properly handle for a long time, its quality is affected due to oxidative deterioration to shorten the oil shelf live.

The iodine value is a measure of the number of grams of iodine (halogen) absorbed by 100 grams of oil sample under specified condition [12]. The decrease of iodine value with change in extraction temperature was investigated by [20] who extracted oil from neem oil using n – hexane at a temperature of 60, 65 and 70 °C and found the iodine values to be 169.40, 167.99 and 162.09 gI₂/100 g respectively and [7] found the iodine values to be 66.58, 65.79 and 61.32 gI₂/100 g at an extraction temperature of 30, 40 and 50 °C respectively. The previous research work showed the decrease of iodine value of neem seed oil as temperature increases. The acid value is defined as the number in milligrams of potassium hydroxide necessary to neutralize the free acid in one gram of the oil. Higher temperature favours higher acid value because temperature affects the hydrolysis of oil [14]. The temperature effect is seen in the previous work of [7] who extracted oil from neem seed using ethanol at 30, 40 and 50 °C with the respective acid values of 32.8, 36 and 40 mg KOH/g; and [20] extracted oil from neem seed using n – hexane at 60, 65 and 70 °C and recorded the acid values as 2.30, 4.94 and 5.48 mg KOH/g respectively. The saponification value is a measure of the average molecular weight of triglycerides in the oil and is the amount of KOH in milligram that is required to saponify the free fatty acid (ester) in the oil [14, 7]. When the extraction temperature increased, more lipids are broken down, thereby increasing the amount of free fatty acid in the oil, which in turn increase the saponification value [7]. The work of [7] on neem oil at 30, 40 and 50 °C gave the respective saponification values as 175.71, 194.20 and 205.85 mg KOH/g; while [15] work on canola cooking oil at 25, 50 and 250 °C and found the saponification values to be 67, 73 and 250 mgKOH/g respectively.

2. MATERIALS AND METHODS

2.1 Materials

The neem seed kernel was obtained from Pankshin Local Government Area of Plateau State in Nigeria in the month of June – July. The extraction of neem seed oil was done using technical grade ethanol solvents (ISO 9001.ISO 14001 certified and manufactured by Mansoura for Resins & Chemical Industries CO.SAE (MRI), Egypt).

2.2 Equipment

Some of the equipment used were solvent extraction plant, ethanol solvent, rotary evaporator, stabilizer, vacuum pump, thermometer, oven, GC – MS and FTIR machines.

2.3 Extraction Procedure

The extraction of neem seed oil was done using technical grade ethanol (99%) as solvents in an extraction plant shown in Figure 1. The plant was adequately checked to be sure all components of the plant are intact and well secured. The electric motor, **C** for stirring the impeller was mounted on the cover of the mixer and the shaft carrying the flat blade turbine impeller connected to it. Valves V1, V2, V3, V4, V5, V6 and V7 were closed. 16.55 kg of ice – block was added to 49.83 litre of water in the reservoir tank, **I** and mercury – in – glass thermometer was used to monitor the temperature at 15 °C. Valve V5 was opened to allow the cooling water pass through heat exchanger, **G** so as to attain cooling stability. This was done to aid condensation of the ethanol vapour to liquid. The main switched was put on to monitor voltage input, which is between 220 – 240 Volts. 1.56 kg of grounded neem seed kernel particle of size 0.42 mm and 19.9 litre of ethanol were charged into the mixer, **B** through V1 and 0.4 liter of ethanol was charged into the washing solvent vessel, **D**. The knobs of the mixer/evaporator heater control and the mixer/timer control were set to positions ‘1’ and ‘1’ respectively on the control panel, **A** to switch – on the electric heater (1000 W) for the mixer and the temperature controller was set to the required temperature and the timer on the control panel, **A** was set to the required contact time of 30 minutes. The set contact time is not activated until the required extraction temperature is attained; the activation of the timing is achieved when the mixer/time control knob is changed to position ‘2’. A period of time was allowed to enable the system stabilize. The stability of the system was confirmed by the aid of a temperature sensor placed in the mixer and a click short sharp sound that would be heard and the appearing of green light on the temperature controller. Once the stability was attained, the electric motor was switched – on and regulated at 77 rpm with the aid of a stirrer speed controller using flat blade turbine impeller which was already connected to the speed control unit and the mixer/timer control is quickly changed to position ‘2’ to start timing and back to position ‘1’ to continue heating. Mixing and agitation commenced immediately for a period of 30 minutes. Once the set time elapses, the heating automatically stopped and stirring continue to avoid settling of

particles. V2 and V4 were opened to allow the mixture of neem cake, neem oil and ethanol to flow into the filtration unit, **E** through the inverted funnel and the stirrer speed controller is turned to zero point. V3 was opened for the washing solvent to flow into the filtration unit for washing the neem cake. Filtration takes place in the filtration unit with the aid of a stainless steel filter mesh of size of 100 μm attached to the cake receiver. The miscella or mixture of neem oil and ethanol flows through the already opened V4 into the evaporator, **F**.

After the cake washing, V4 was closed and the filtration unit was opened to collect the cake receiver and the mixer was opened to collect any cake left over in the mixer. The total cake in the receiver was placed in an oven for drying the cake. The drying was done using oven manufactured by SANFA Limited, England; Model NO: DHG – 9030 with temperature range of 50 °C to 200 °C at the boiling temperature of the solvent, 78 °C. The weight of the cake was taken after every 20 minutes until constant weight was obtained to determine the percentage yield. Valves V1, V2, V3 and V4 were shut and the knob of the mixer/evaporator heater control was set to position ‘2’ to switch – on the evaporator heater (1000 W). The evaporator temperature controller was set to the recovery temperature of the neem oil and the vacuum pump, **K** in conjunction with pressure gauge, **M** and step – down transformer, **J** were adjusted to the required vacuum pressure for separation of the oil from the miscella under vacuum condition. The ethanol vapour passed through the already cooled 1 – 2 shell – and – tube heat exchanger (condenser) and was collected in the condensate receiver, **H** as liquid solvent. After 3 hours 30 minutes of evaporation without vacuum pump and 2 hours 45 minutes under vacuum condition; a sample of oil was collected via V6 and analyzed using pH meter. Based on the viscous physical appearance of the product (neem oil) and the pH value, the evaporator heater was switched off by turning the knob of the mixer/evaporator heater control to position zero, the main switch was put off and V6 was closed. The collected neem oil at 78 °C was dried in an oven at 78 °C for 20 minutes to remove any residual ethanol and the neem oil obtained at 50, 55 and 60 °C were further dried using rotary vacuum evaporator at the respective temperatures to remove any residual ethanol. V7 was opened to collect the recovered solvent for recycling.



Figure 1: Scaled up solvent extraction plant

3. RESULTS AND DISCUSSIONS

3.1 Effect of Temperature on the Quality of Neem Seed Oil

The iodine, acid and saponification values of the extracted neem oil at different temperatures/vacuum pressures are shown in Table 1.

Table 1: Effect of temperature on iodine, acid and saponification values of neem seed oil extracted using ethanol as solvent

Temperature (°C)	Iodine Value (gI ₂ /100g)	Acid Value (mg KOH/g)	Saponification Value (mg KOH/g)
ME (20)	62.70	3.4	158.74
50/280 mbar	63.39	3.7	161.70
55/373 mbar	61.02	3.9	194.10
60/467 mbar	60.30	4	199.78
E78	60.10	4.2	210.18

The quality of the extracted neem oil varies with increase of extraction temperatures. The iodine, acid and saponification values at 20, 50, 55, 60 and 78 °C were 62.70, 63.39, 61.02, 60.30 and 60.10 gI₂/100g; 3.4, 3.7, 3.9, 4 and 4.2 mg KOH/g; 158.74, 161.70, 194.10, 199.78 and 210.18 mg KOH/g respectively as seen from Table 1. When the extraction temperature increased from 20°C to 78°C, the iodine value decreased from 62.70 to 60.10 gI₂/100g due to auto – oxidation reaction which leads to formation of non – radical products [16]. Increase in extraction temperature results in the loss of unsaturation (double or triple bonds) in the fatty acids of the oil and this leads to decrease in iodine value due to loss of bonds in the oil. Higher iodine value indicates higher degree of unsaturation, which contribute to the functionality and reactivity of the oil. The double bonds and the carboxylic ends provide sites for crucial industrial reaction as reactions are carried out on the double bonds of the unsaturated glycerides. The conversion made the oil less or non – reactive, that is good for long term storage. The double bond in the oil provide the active site and once the double bond is converted to single bond the oil becomes less or non – reactive. Neem oil with lower iodine value is good for long term storage before usage due to its saturated condition [13]. Authors such as [20, 7] investigated and showed the decrease of iodine value of neem seed oil as temperature increases. Acid value indicates the level of free fatty acid in the oil and increase of extraction temperature brings about decomposition of triglyceride into fatty acid [7]. The acid value increases from 3.4 to 4.2 mg KOH/g as seen from Table 1. The increase of extraction temperature from 20 to 78°C brings about the formation of more fatty acid in the oil. The increase of acid value due to increase of extraction temperature of oil from neem seed is correlated with the passed work of [21, 7, 20]. The saponification value increases from 158.74 to 210.18 mg KOH/g and is the amount of KOH in milligram that is required to saponify the free fatty acid (ester) in the oil [14, 7]. When the extraction temperature increased, more lipids are broken down, thereby increasing the amount of free fatty acid in the oil, which in turn increase the saponification value [7]. Higher saponification values are indicative of the presence of lower molecular weight compounds/short chain fatty acids in the oil. Higher saponification value is more desirable when considering oil for soap industry and undesirable for production of biodiesel [13]. This finding is in agreement with those reported by [15, 13, 7].

The trend of value associated with the decrease of iodine value, increase of acid and saponification values due to increase of temperature agreed with the work of [13] on Parinari seed oil, [21, 7] on neem seed oil. Therefore, the neem oil with low reactivity in term of lower iodine value and high saponification value is good for soap production after further reduction of the acid value.

3.2 Effect of Temperature on the Fatty Acid Structures of Neem Seed Oil

Chromatographs of the neem seed oils were obtained using GC – MS for the mechanical expressed oil at ambient temperature of 20 °C and solvent extracted oil at 50 °C/280 mbar, 55 °C/373 mbar, 60 °C/467 mbar, and 78 °C obtained from the miscella. The components identification and chromatograph of the neem oil obtained at 78 °C are shown in Figures 2 and 3 respectively. The calculations for percentage compositions of the fatty acid structures of the 78 °C oil are shown in Table 2.

MULTI-USER SC. RES. LAB. ABUZ						
Library Search Report						
Data Path : D:\MassHunter\GCMS\1\5977\Abdul\JOHN GOJI USMAN\						
Data File : JOHN GOJI USMAN2.D						
Acq On : 19 Apr 2023 16:10						
Operator : Multi-User Science Research Laboratory						
Sample : E78oC						
PK#	RT	Area%	Library/ID	Ref#	CAS#	Qual
1	13.692	0.15	D:\MassHunter\Library\NIST14.L			
			Hexadecanoic acid, methyl ester	130813	000112-39-0	98
			Hexadecanoic acid, methyl ester	130822	000112-39-0	97
2	14.724	0.28	D:\MassHunter\Library\NIST14.L			
			Pentadecanoic acid, 14-methyl-, methyl ester	130843	005129-60-2	97
			n-Hexadecanoic acid	117418	000057-10-3	98
3	16.097	3.58	D:\MassHunter\Library\NIST14.L			
			n-Hexadecanoic acid	117419	000057-10-3	97
			n-Hexadecanoic acid	117416	000057-10-3	83
4	16.657	0.69	D:\MassHunter\Library\NIST14.L			
			11-Octadecenoic acid, methyl ester	155737	052380-33-3	99
			10-Octadecenoic acid, methyl ester	155731	013481-95-3	99
5	17.102	5.90	D:\MassHunter\Library\NIST14.L			
			cis-13-Octadecenoic acid, methyl ester	155747	1000333-58-3	99
			n-Hexadecanoic acid	117419	000057-10-3	95
6	17.964	5.44	D:\MassHunter\Library\NIST14.L			
			Methyl stearate	157879	000112-61-8	87
			Methyl stearate	157882	000112-61-8	70
7	17.964	5.44	D:\MassHunter\Library\NIST14.L			
			n-Hexadecanoic acid	117418	000057-10-3	99
			n-Hexadecanoic acid	117419	000057-10-3	96
8	17.964	5.44	D:\MassHunter\Library\NIST14.L			
			Tridecanoic acid	78016	000638-53-9	93
			cis-Vaccenic acid	142073	000506-17-2	95
9	17.964	5.44	D:\MassHunter\Library\NIST14.L			
			Oleic Acid	142071	000112-80-1	95
10	17.964	5.44	D:\MassHunter\Library\NIST14.L			
			trans-13-Octadecenoic acid	142094	000693-71-0	95

Figure 2: Components identification of neem oil obtained at 78 °C from the miscella

Peak No.	Retention Time (min)	Retention Time (min)	Retention Time (min)	Library Name	Library ID	Library ID	Library ID
7	18.177	5.90	D:\MassHunter\Library\NIST14.L	Oleic Acid	142071	000112-80-1	95
				trans-13-Octadecenoic acid	142094	000693-71-0	95
				cis-Vaccenic acid	142073	000506-17-2	96
8	18.697	9.52	D:\MassHunter\Library\NIST14.L	cis-13-Octadecenoic acid	142083	013126-39-1	95
				trans-13-Octadecenoic acid	142094	000693-71-0	93
				n-Hexadecanoic acid	117418	000057-10-3	99
9	19.400	5.78	D:\MassHunter\Library\NIST14.L	n-Hexadecanoic acid	117419	000057-10-3	96
				Tridecanoic acid	78016	000638-53-9	93
				Oleic Acid	142070	000112-80-1	95
10	19.847	4.68	D:\MassHunter\Library\NIST14.L	cis-13-Octadecenoic acid	142083	013126-39-1	95
				cis-Vaccenic acid	142073	000506-17-2	95
				Oleic Acid	142071	000112-80-1	94
11	20.379	6.79	D:\MassHunter\Library\NIST14.L	Cyclopropaneoctanal, 2-octyl-	140252	056196-06-6	72
				Oleic Acid	142069	000112-80-1	66
				2-Methyl-E,E-3,13-octadecadien-1-o	140255	1000130-90-6	60
12	21.389	4.61	D:\MassHunter\Library\NIST14.L	cis-Vaccenic acid	142073	000506-17-2	95
				9-Octadecenoic acid, (E)-	142089	000112-79-8	90
				Oleic Acid	142069	000112-80-1	87
13	22.659	5.48	D:\MassHunter\Library\NIST14.L	Oleic Acid	142070	000112-80-1	95
				cis-Vaccenic acid	142073	000506-17-2	95
				trans-13-Octadecenoic acid	142094	000693-71-0	94
14	23.671	4.45	D:\MassHunter\Library\NIST14.L	Oleic Acid	142070	000112-80-1	96
				cis-Vaccenic acid	142073	000506-17-2	95
				Oleic Acid	142069	000112-80-1	95
15	25.580	4.40	D:\MassHunter\Library\NIST14.L	Cyclopropaneoctanal, 2-octyl-	140252	056196-06-6	72
				Oleic Acid	142069	000112-80-1	66
				2-Methyl-E,E-3,13-octadecadien-1-o	140255	1000130-90-6	60
16	26.736	0.21	D:\MassHunter\Library\NIST14.L	Supraene	243217	007683-64-9	96
				Squalene	243218	000111-02-4	92
				Squalene	243216	000111-02-4	91
17	27.515	3.13	D:\MassHunter\Library\NIST14.L	cis-Vaccenic acid	142073	000506-17-2	78
				Oleic Acid	142070	000112-80-1	74
				1,2-Benzisothiazole, 3-(hexahydro-1H-azepin-1-yl)-, 1,1-dioxide	12		
18	29.851	6.84	D:\MassHunter\Library\NIST14.L	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	210562	000111-0	
				9-Octadecenoic acid (Z)-, 2-hydrox	210570	003443-84-3	64
				y-1-(hydroxymethyl)ethyl ester	142076	1000190-13-7	45
19	32.136	4.14	D:\MassHunter\Library\NIST14.L	Trimethylsilyl-di(trimethylsiloxy)-silane	140353	139347-50-5	44
				6-Octadecenoic acid, (Z)-	142084	000593-39-5	43
				1,2,5,6-Di-O-isopropylidene-3-O-methanesulfonyl glucofuranose	1947		
20	34.442	6.20	D:\MassHunter\Library\NIST14.L	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	210562	000111-0	
				Butyl 9-octadecenoate or 9-18:1	195600	1000336-74-7	25
				2-Ethylacridine	71643	055751-83-2	20
21	34.881	4.12	D:\MassHunter\Library\NIST14.L	Octadecanoic acid	144272	000057-11-4	56
				Octadecanoic acid	144269	000057-11-4	44
				Hexasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-	250548	00099	
22	36.885	7.71	D:\MassHunter\Library\NIST14.L	Octadecanoic acid	144269	000057-11-4	53
				2-Ethylacridine	71643	055751-83-2	38
				3,5-Dimethylbenzaldehyde thiocarbamoylhydrazone	71186	1000195-15-	

Figure 2: Components identification of neem oil obtained at 78 °C from the miscella (cont'd)

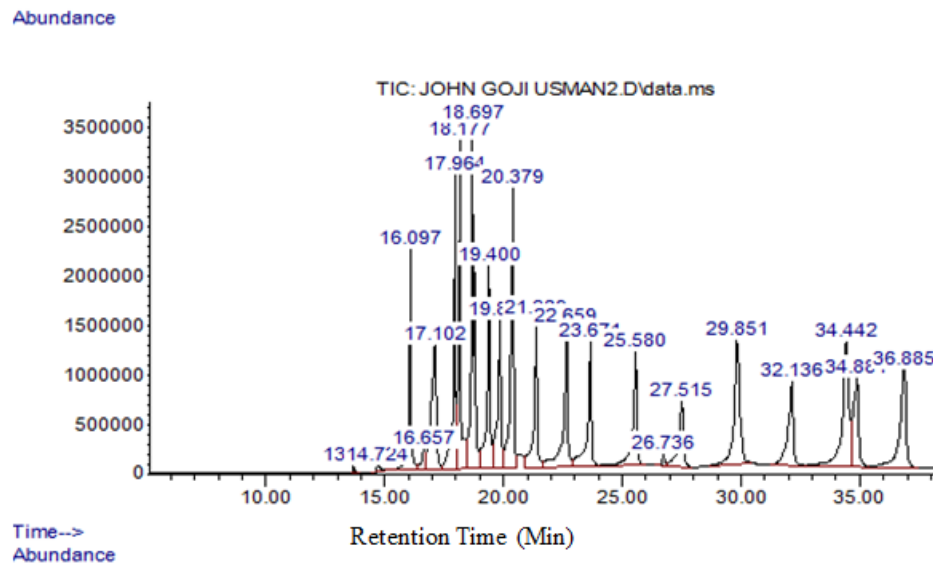


Figure 3: The Chromatograph of oil obtained at 78 °C

Table 2: Identification and calculation of polysaturated, monounsaturated and saturated compositions of neem oil obtained at 78 °C from the Miscella.

Structure			Total (%)
Polyunsaturated	Peaks	16	0.21
	% composition	0.21	
Monounsaturated	Peaks	3,6,7,9,10,12,13,14,17,18 and 20	56.09
	% composition	3.58+5.44+5.90+5.78+4.68+4.61+5.48+4.45+3.13+6.84+4.14+6.20	
Saturated	Peaks	1,2,4,5,8 ,11, 15, 19,21 and 22	43.70
	% composition	0.15+0.28+0.69+5.90+9.52+6.79+4.40+4.14+4.12+7.71	
Total			100

The percentage compositions of the fatty acid structure for the oils are shown in Tables 3.

Table 3: Percentage composition of polyunsaturated, monounsaturated and saturated fatty acids in the extracted neem oil at different temperature and respective vacuum pressure

Sample	Polyunsaturated (%)	Monounsaturated (%)	Saturated (%)	Non – oil component (%)
ME (20°C)	21.58	55.88	22.54	–
50°C/280 mbar	6.33	57.96	35.53	–
55°C/373 mbar	3.09	55.32	41.59	–
60°C/467 mbar	1.83	51.80	46.37	–
78°C	0.21	56.09	43.70	–

Auto – oxidation is a spontaneous reaction between molecular oxygen and the unsaturated lipids (unsaturated fatty acids) via free radical mechanism to form lipid hydro – peroxide [25]. Auto – oxidation played a very important role in the conversion of polyunsaturated components to monounsaturated components and finally to saturated components.

From Table 3, the polyunsaturated component is very high in the mechanically expressed oil (ME) at 20 °C with a value of 21.58%. The gradual reduction of the polyunsaturated component to 0.21% at 78 °C can be attributed to auto – oxidation reaction of the lipid. At 50 °C, there is increase of monounsaturated components from 55.88% in mechanical expressed oil to 57.96% in the 50 °C oil. This increment was due to the reduction of polyunsaturated component in ME from 21.58% to 6.33% in the 50 °C due to change of temperature from 20 °C to 50 °C. the auto – oxidation reaction is greatly assisted by temperature increase as opined by [26] that auto – oxidation of lipid is aided by increase of temperature. The autoxidation of neem oil is a continuous free radical chain reaction [16] that will lead to continuous and simultaneous formation of monounsaturated and saturated fatty acids. The decrease of polyunsaturated components to saturated components is similar to the work of [15] on canola cooking oil where the researchers only states reduction of

polyunsaturated components to saturated component without stating the percentage conversion. The reduction of polyunsaturated components can be attributed to auto – oxidation reaction of the oil that led to formation of non – radical products (saturated components). The neem oil extracted at 78 °C has the lowest percentage of polyunsaturated components and therefore less reactive. The oil can be stored for longer time before usage when compare to other oil with higher percentage of polyunsaturated component obtained at other temperatures. The chromatograph of the oil obtained at 78 °C is shown in Figure 3 and the GC – MS identified fatty acid composition of the 78°C oil is shown in Table 4.

Table 4: Fatty acid compositions of neem oil obtained at 78°C from the miscella

S/NO	Component	Total (%)	Uses
1	Oleic acid (Monounsaturated)	46.61	Detergent, soap and cosmetics
2	Stearic acid (Saturated)	11.83	Soap, cosmetics and pharmaceutical
3	Palmitic acid (Saturated)	16.54	Soap
4	11 – Octadecenoic acid (Monounsaturated)	3.58	Pharmaceutical
5	Cis – Vaccenic acid (Monounsaturated)	5.90	Pharmaceutical
6	Cyclopropanoic acid (Saturated)	11.19	Pharmaceutical
7	Squalene (Polyunsaturated)	0.21	Cosmetics
8	Trimethylsilyl – di(trimethylsiloxy)- silane (Heavily saturated)	4.14	–
Total		100	

The components found in Chromatograph of the oil obtained at 78°C from the Miscella as shown in Figure 3 are clearly indicated by the peaks in Figure 2. The 22 peaks associated with the 78°C oil contain eight components in the oil and the percentage composition of the components is shown in Table 4. The percentage compositions of the fatty acid structure associated with the 78°C oil are Polyunsaturated, 0.21%; Monounsaturated, 56.09% and Saturated, 43.70%. Based on the composition of the fatty acid, the neem oil can be used for production of soap, cosmetics and pharmaceutical.

3.3 FT – IR RESULT

The FT – IR was conducted within the frequency range of 4 000 – 750 cm⁻¹ and a wavenumber precision of 0.1 cm⁻¹ using KBr in an Agilent Technologies CARY 630 FT – IR machine. The spectrum of 78°C neem seed oil is shown in Figure 4.

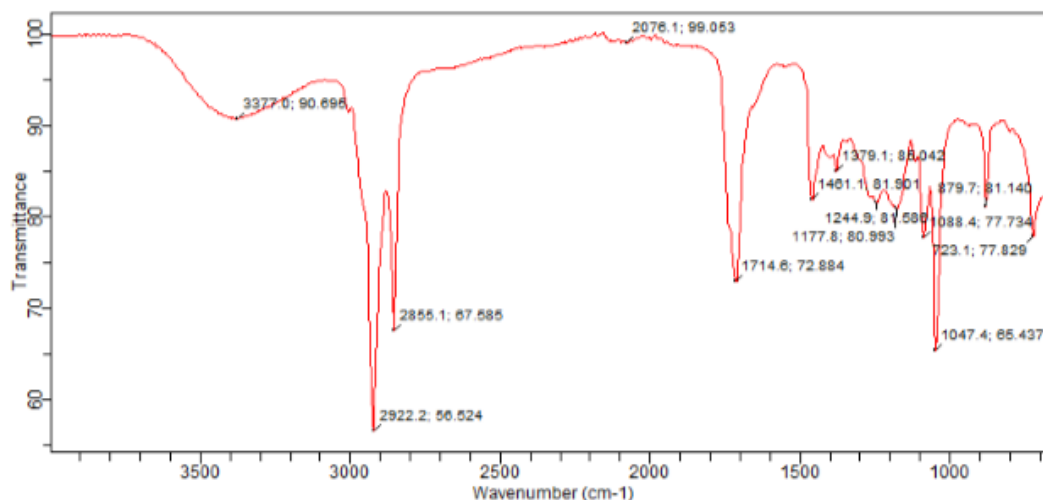


Figure 4: FT – IR spectral analysis of E78 neem seed oil at a frequency of 4000 – 750 cm⁻¹.

Considering the dominant peaks from the transmission spectra of Figure 4, the following frequency bands identified were 2922.2, 2855.1, 1714.6, 1177.8, 1047.4 and 723.1 cm⁻¹ and the respective associated functional groups were C – H (Alkane), C – H (Alkane), C = O (Aromatic), C – C (Alcohol), C – O (Alcohol) and C – H (Aromatic). The alkane contains C – H and C – C bonds. The C – H stretching in aliphatic hydrocarbon appears in the 3 000 – 2800 cm⁻¹ band range (Stuart, 2004). The 2922.2 and 2855.1 frequencies bands fall within the range of the aliphatic hydrocarbon functional group (C – H) compound and suggest the presence of alkane or alkyl group. The FTIR result confirmed the GC – MS result of the presence of saturated component in the neem oil recovered at 78 °C. These findings are similar to the work of [1] on neem oil, where they found the C – H symmetric stretch of methyl group at the absorption peaks of 2923.78 and 2855.25 cm⁻¹. The frequency band of 1714.6 cm⁻¹ falls within the range of 1730 – 1705 cm⁻¹ which confirmed the presence of C = O stretching carbonyl functional group of aromatic esters [22] and this suggests the presence of ketone or aldehydes. The C –

O stretching of alcohol and phenol are strongly found within 1300 – 1000 cm^{-1} of the frequency band and the 1177.8 and 1047.4 cm^{-1} frequency bands fall within the range and constitute the presence of C – O stretching functional group in the oil (Stuart, 2004). This agreed with the work of [1], where the researchers found C – O stretch at a peak value of 1095.86, 1236.83, 1106.38 and 1236.83 cm^{-1} which fall within the range of 1300 – 1000 cm^{-1} . The C – H bending band of aromatic compound appears in the 900 – 690 cm^{-1} (out – of – plane bending) range (Stuart, 2004). The 723.1 cm^{-1} frequency band indicates the presence of an aromatic compound in the oil. The aromatic compounds are use in pharmaceutical industries for drug manufacturing and for antiseptics production. The functional groups identified agreed with the findings by [1, 23].

The FTIT identified the functional groups as bio – active components that are useful for application in pharmaceutical, cosmetic and soap industries. There is no transmittance between the ranges of 2220 – 2260 cm^{-1} . This indicates the absent of cyanide groups in the extracted oil, which shows that the oil is non – toxic substances [24].

4. CONCLUSION AND RECOMMENDATION

4.1 Conclusion

The quality of the extracted neem oil varies with increase of extraction temperatures. The iodine, acid and saponification values at 20, 50, 55, 60 and 78 °C were 62.70, 63.39, 61.02, 60.30 and 60.10 $\text{gI}_2/100\text{g}$; 3.4, 3.7, 3.9, 4 and 4.2 mg KOH/g; 158.74, 161.70, 194.10, 199.78 and 210.18 mg KOH/g respectively. The mechanically expressed oil has the highest percentage composition of polyunsaturated components of 21.58% and lowest saturated percentage composition of 22.54%; while the 78°C oil has the lowest percentage composition of polyunsaturated component of 0.21% and relative highest percentage composition of saturated component of 43.70%. The major fatty acid composition found in the 78°C oil are: Oleic acid, 46.61%; Stearic acid, 11.83%; Palmitic acid, 16.54% and Cyclopropaneoctanal, 11.19%. The functional groups identified in the oil 78°C oil were C – H (Alkane), C = O (Aromatic), C – C (Alcohol), C – O (Alcohol) and C – H (Aromatic). Based on the lowest iodine value, lowest percentage of polyunsaturated component and high percentage of saturated components the neem oil recovered at 78 °C is considered as the high grade neem oil because it can be stored for a long time before usage due to its less reactivity. The oil is non – toxic due to the absent of cyanide group and safe for applications. Based on the composition of the fatty acid , the neem oil is recommended for production of soap, cosmetics and pharmaceutical.

4.2 Recommendation

The solvent – solute ratio should be investigated using the same extraction plant. The thermodynamic and kinetic studies of the leaching process should be studied using the same extraction plant.

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