JEAS
Journal of Engineering and Applied Sciences 13 (2018), 25-39

JOURNAL OF ENGINEERING
AND
APPLIED SCIENCES

Solvents comparative extraction performance for the synthesis of potential *Terminalia catappa* transformer oil

Chinedu M. Agu[1*], Matthew C. Menkiti[1], Albert C. Agulanna[2] and Innocent E. Nweke[3]

[1] Chemical Engineering Department, Nnamdi Azikiwe University, Awka, Nigeria.
[2]Materials and Energy Technology Department, Projects Development Institute (PRODA), Emene Industrial Area, Enugu, Nigeria.
[3] Transmission Company of Nigeria (TCN), Onitsha Sub-region, Anambra State, Nigeria.
[*]CorrespondingAuthor's E-mail: eduetal@yahoo.com

Abstract
This work focuses on the extractive influence of n-hexane and petroleum ether on *Terminalia catappa K*ernel (TCK) oil yield. The TCK oil were characterized using standard methods, Gas chromatographic (GC) and Fourier transform infrared (FTIR) analyses. Results indicated that time and particle size effects were significant while temperature was not. Pseudo-second order kinetic model fits more suitably, compared to hyperbolic model. The process Gibbs free energy, entropy and enthalpy values at 55°C for n-hexane and petroleum ether were -28.76KJ/mol, 0.643KJ/mol, 182.81KJ/mol and -30.42KJ/mol, 0.686KJ/mol, 195.18KJ/mol ,respectively, indicating spontaneous, irreversible, and endothermic process. N-hexane gave optimally higher oil yield of 60.45 % at 55 °C, 0.5 mm and 150 min.

Keywords:*Terminaliacatappa L.*, Solvent extraction, Kinetics, Thermodynamics

1. Introduction

TerminaliacatappaL. (TC) kernel is one of the oldest known kernels obtained from ornamental TC tree. Its tree belongs to the combretaceae family and was believed to have originated from Malaysia. This tree is often found in wet coastal regions and is well distributed in the tropics as well as in the tropical America (Adeolu, 2013). In Nigeria, it is mostly found in the south, especially in the south-east where they are mainly planted for ornamentalpurposes with little or no attention to the consumption/utilization of the fruit and kernel (Ezeokonkwo and Dodson, 2004). Thus, it is non-food competing and would be needful to evaluate the potential application of the kernel oil, specifically as a raw material for industrial production of transformer oil(Agu, 2014).

Terminaliacatappa L. kernel (TCK) is known for relatively high oil yield, but it is still highly underutilized for both domestic and industrial purposes. The oil content of the kernels varies and ranges from 49 to 64% (Agu, 2014; Iha et al., 2014; Dos Santos et al., 2008; Monnet et al., 2012). It is also rich in protein and carbohydrate, the percentage of which ranges from 17% to 18.39% and 25.61%, respectively (Adepoju et al., 2014). Terminaliacatappa L. contains huge quantity of fatty acid. The total saturated fatty acid content was reported to be 34.2%, while the total unsaturated fatty was 64.5% (Iha et al., 2014).

However, in other to extract oil from TCK, a number of extraction methods need to be evaluated prior to the choice of the method to be used. Generally, several methods are available for the extraction of oil from plants, seeds and nuts. Of these techniques, solvent extraction method is the most commonly used due to its relative simplicity and cost effectiveness (Azmir et al., 2013). The oil yield in solvent extraction is highly dependent on a number of factors that includesolvent type, extraction temperature, solute particle size(Azmir et al., 2013; Atabani et al., 2013). Other factors include agitation speed, extraction time and solute to solvent ratio (Agu, 2014; Rakotondramasy-Rabesiaka et al., 2008; Vetal et al., 2012).

Furthermore, oil extraction kinetics is important in the design of effective solvent extraction processes. The common kinetic models used in solid-liquid extractions includes but not limited to Fick's law of diffusion (Cacace and Mazza, 2003), unsteady diffusion (Stankovic et al., 1994), film theory (Pekic et al., 1988) and empirical models (Peleg, 1988).

Presently,there is no comparative literature information on thethermodynamics, kinetic and efficiencyof*Terminaliacatappa L.* kernel oil extraction using both n-hexane and petroleum ether. Therefore, this work elicits interest in closing these gaps.Furthermore, physicochemical properties of the oil were examined,while its fatty acid composition and prevalent functional groups were evaluated using gas chromatography (GC) and Fourier Transform Infrared (FTIR), respectively, with a view of evaluating its potential application as TO.Additionally, obtained experimental kinetic data were fitted to two selected extraction kinetics (pseudo second order and hyperbolic) models. In addition, the degree of correlation of the models to the experimental kinetic data was estimated using correlation coefficient (R^2),root mean square error (RMS) and standard deviation (SD).

Theory

Two kinetic models were selectively studied: hyperbolic and pseudo second order models equations 1 and 2, respectively. The nonlinearandlinearkinetic equations of these models were presented in Table 1. In order to apply these models, a number of assumptions were made with respect to solid-liquid extraction process. These assumptions include:

- Grinded kernel particles are isotropic in nature and are of uniform size;
- Distribution of extracted oils within the milled kernel particles is even and varied with time only;
- Diffusion coefficient of the extracted oils is constant;
- Net diffusion occurs specifically towards the external surface of the seed particles (Kitanovic et al., 2008).

Table 1: Models names and descriptive non-linear and linear equations

Kinetic Models	Nonlinear Eqs.	Linear Eqs.	
Hyperbolic	$\bar{q} = \frac{C_1 t}{1 + C_2 t}$	$\frac{1}{\bar{q}} = \frac{1}{C_1} \times \frac{1}{t} + \frac{C_2}{C_1}$	(1)
Pseudo 2nd Order	$\bar{q} = \frac{C_s^2 kt}{1 + C_s kt}$	$\frac{t}{C_t} = \frac{t}{kC_s^2} + \frac{t}{C_s}$	(2)

2.0 Material and methods

2.1 Materials

TC seeds were collected from Umuaga, Enugu State, Nigeria. N-hexane, petroleum ether (with boiling point range of 60 to 80°C) and other chemicals of analytical grades were procured from a chemical vendor in Enugu. The reagents were used without further purification.

2.2 Methods

2.2.1 Sample preparation

The TC seeds external coatings were carefully cracked and the kernels were removed and cleaned. The kernels were then oven dried to a constant weight at 60°C for 24 h. Manual hand grinder was then used to grind the kernels and separated with five different sieve plates of sizes: 0.5 mm, 1.0 mm, 1.5 mm, 2.0 mm, and 2.5 mm to obtain 5 different average particle sizes of 0.5 mm, 1.0 mm, 1.5 mm, 2.0 mm and 2.5 mm, respectively.

2.2.2.Solvent Extraction of TCK oil

Soxhlet oil extraction from the kernels (5 particle sizes) was carried out in line with the Association of Official Analytical Chemists (AOAC) 963.15 method (AOAC, 1990) as adapted by Menkiti et al., (2015).Solvents used were n-hexane and petroleum ether. For each case of parameter under consideration, the extraction cycle was carried out in triplicate (For one factorat a time) and the average oil yield obtained using equation 3.

$$\%\, Oil\ yield\ = \frac{weig\,ht\ of\ oil\ extracted\ \ (g)}{weig\,ht\ of\ TC\ kernel\ \ (g)} \times 100 \tag{3}$$

2.3Physicochemical Characteristics of TC kernel oil

Crude *Terminaliacatappa L*. kernel (TCK) oil extract was used for the analyses. Acid value (AOAC 969.17), iodine value (AOAC 993.20) and oil density (AOAC 985.19), were determined in line with AOAC approved techniques (AOAC, 1990). Dielectric strength and viscosity were measured according to IEC 60156 (2003) and ASTM D445 (2011) standard methods, respectively. Each measurement was done in triplicate and the average values reported.

2.4Fatty acid composition of TC kernel oil

The fatty acid profile of TC kernel oil was determined in line with AOAC 996.06 method (AOAC, 1990). The method involves the identification of the fatty acid methyl esters with gas chromatography unit (Model 910) that was equipped with a flame ionization detector and integrator. In this equipment, the injector and detector temperature was 250°C, while the oven temperature was kept at 190°C for 15 min and afterwards increased to 230°C at the rate of 5°C/min for 15min. The carrier gas used was nitrogen and was kept at a pressure of 500 kPa. The identified fatty acid methyl esters were compared with standard compounds. The quantity of each fatty acid was assessed from the percentage area of the individual fatty acid methyl ester (Zahedi and Azarpour, 2011; Liu et al., 2009; Azmir et al., 2014; Menkiti et al., 2015). The analysis was also conducted in triplicate and the average value was noted.

2.5FTIR analysis

The FTIR analysis of the TC kernel oil sample was carried out using BUCK Scientific Infrared Spectrophotometer Model 530. The measurements were obtained between 4000 and 400cm^{-1}.

2.6 Statistical fitting criteria for the kinetic models

The fittingof the kinetic models studied was statistically evaluated using coefficient of determination (R^2),RMS (Equations 4) (Kitanovic et al., 2008), and SD (Equation 5) (Rahmanian., et al., 2011).

$$RMS\ =\ \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{\bar{q}_{exp}\ -\bar{q}_{cal}}{\bar{q}_{exp}}\right)^2} \tag{4}$$

$$SD\ =\ \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(\left|\frac{\bar{q}_{\exp(i)}-\bar{q}_{cal\,(i)}}{\bar{q}_{\exp(i)}}\right|\ -AARE\right)^2} \tag{5}$$

Absolute average relative error (AARE) was calculated using equation 6.

$$AARE\ =\ \frac{1}{N}\ \times\ \sum_{i=1}^{N}\left(\left|\frac{\bar{q}_{\exp(i)}-\bar{q}_{cal\,(i)}}{\bar{q}_{\exp(i)}}\right|\right) \tag{6}$$

The higher the value of R^2 and the lower the values of the RMS and SD; the better will be the goodness of fit (Kitanovic et al., 2008).

2.7Thermodynamics parameters

Thermodynamic parameters: enthalpy, entropy and Gibbs free energy changes (ΔH, ΔS and ΔG, respectively) were, respectively calculated using Eqs. 7-8 (Liauw et al., 2008).

$$\Delta G = -RTIn\,K \quad (7)$$

$$In\,K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)$$

Where K is equilibrium constant, T equilibrium temperature, R is gas constant (8.314J/mol K).

3.0 Results and Discussions

3.1 TCKOil yield

The oil yields obtained using n-hexane and petroleum ether were found to be 60.45 and 56% (in mass), respectively. These results could be attributed to polarity of the solvents, with the former having lesser polarity index than the later (Menkiti et al., 2015).Theseresults are higher when compared to that reported for cottonseed (Khan et al., 2010), and soybean (Lawson et al., 2010) thus, signifying a potential economic benefit for industrial application,specifically as base oil for transformer fluid production. However, oil yield of 50% (in mass) for TCK was reported by Iha et al. (2014). This difference between the oil yield reported by Iha et al. (2014) and that obtained in this work could be attributed to factors such as geographical location, seed variety, and harvest period (Ejikeme et al., 2010).Furthermore, the higher oil yield recorded for n-hexane could be attributed to its more non-polar property when compared to that of petroleum ether (Menkiti et al., 2015). This non-polar property facilitated easier penetration of n-hexane(as against petroleum ether) into the matrix of the kernel particles during extraction (Sulaiman et al., 2013; Agu, 2014).

3.2 Physicochemical characteristics of TC kernel oil

Table 2 shows some important physicochemical properties of TCK oil. It could be seen that the viscosity of TC kernel was lower than that reported byIha et al.(2014) and Dos santos et al. (2008). However, the acidity of TCK oil in this work was higher than that reported byDos santos et al. (2008) but lower than that reported by Iha et al. (2014) for the same oil. This lower acid value when compared to the result obtained by Iha et al; (2014),could be attributed to the breed of *Terminaliacat/appa L*. TCK oil in this work had higher iodine value (IV) than 83.92 g/I_2/100g oil reported by Dos Santos et al., (2008). This was an indication of the high level of saturation in the oil as presented in Table 3. The density of TCK oil sample in Table 2 was 890g/cm^3. This was lower than that reported by Iha et al., (2014) for TCK oil. Furthermore, the dielectric strength (DS) value of TCK oil was 30.61 KV. Dielectric strength is defined as the maximum electric field that a pure substance can withstand under ideal conditions without experiencing failure of its insulating properties (Derick et al., 2014). The DS value of TC kernel oil was lower than that of soybean oil (39 KV) but higher than that of palm kernel oil (25 KV) reported elsewhere by Usman et al. (2012). However, this value could be improved with further purification and transesterification to obtain modified TCK oil which could be used as transformer fluid (Menkiti et al., 2017; Agu, 2014). In addition, the introduction of natural antioxidant additives would further improve the DS of modified TCK oil (Agu, 2014).

Table 2: Physicochemical properties of TCK oil

Property	Unit	TO Spec.	TCKO	Standard method
Oil Yield	%	—	60.45	AOAC 926.12
Dielectric strength	KV	40 - 60	30.61	IEC 60156
Viscosity, 40 °C	mm^2 s^{-1}	10	20.29	ASTM D445
Acid value	mg KOH/g	<0.01	4.73	AOCS 969.17
Density, 20°C	g cm^{-3}	870	890	ASTM D1298
Iodine value	g/I_2/100g oil	—	101.86	AOCS CD 1c-85

-Not reported, TO Transformer oil, Spec., Specifications.

3.3 Fatty acid composition of TC kernel oil

Fatty acid composition of the TC kernel oil was determined by GC and is presented in Table 3. Table 3 shows that TCK oil was composed of over 40% saturated fatty acid when compared to approximately 34% reported by Iha et al. (2014). The mono-unsaturated and poly-unsaturated fatty acids present in TCK oil were 33.25% and

22.85% respectively. The result of the fatty acid composition for TC kernel oil obtained in this work was in close agreement with those reported by Iha et al., (2014) and Dos santos et al., (2008). Furthermore, Table 3indicates that TCKoil had lauric acid as well as high level of other saturated fatty acid, unlike that reported by Iha et al., (2014) and Dos santos et al., (2008) where lauric acid was not present. This could most likely be due to factors such as geographical location and variety (Ejikeme et al., 2010).

Table 3: Fatty acid composition of *Terminaliacatappa L.*

Fatty acid	TCK oil
C12:0 (Lauric acid)	0.94
C14:0 (Myristic acid)	0.54
C16:0 (Palmitic acid)	36.01
C16:1 (Palmitoleic acid)	–
C18:0 (Stearic acid)	6.4
C18:1 (Oleic acid)	33.25
C18:2 (Linoleic acid)	22.26
C18:3 (Linolenic acid)	0.59
Saturated fatty accids (%)	43.89
Mono-unsaturated fatty acid (%)	33.25
Poly-unsaturated fatty acid (%)	22.85

– Not present

3.4 FTIR analysis

Fig. 1 shows the FTIR spectrum of TCK oil. The FTIR result was analyzed and comparewith known signature of identified materials (Barbara, 2004). The spectrum indicated 6 discernable peaks at frequency range of 4000 to 400cm^{-1}. The peak ranges that were centered at 3474.88 cm^{-1} and 3305.14 cm^{-1} are characteristics of O–H stretching which indicated the presence of water. The peak range centered at 2929.00cm^{-1} was a characteristic of C – H stretching, which indicated the presence of fats and carbohydrate. Also, the peak at 2868.24cm^{-1} was characteristics of C = H stretching, which depicted the presence oxygen-containing compounds (Aldehydes and Ketones). Furthermore, the peak at 2344.55cm^{-1} was a characteristic combination N – H stretching, associated with amine species, as could be confirmed by the presence of Nitrogen. Similarly, the peak at 2036.90cm^{-1} was characteristics of O – H stretching, thus showed the presence of organic molecules and compounds. The presence of C–H and O–H linked to fats/oil indicated the potentials for TCKO utilization as transformer fluid. This could be attributed to the abundance of biodegradable vegetable oil from TCK that could be modified as transformer fluid (Menkiti et al., 2017). Also the following groups: C–H, C=H, N–H, and O–H found in TCKO showed biodegradability of the oil.

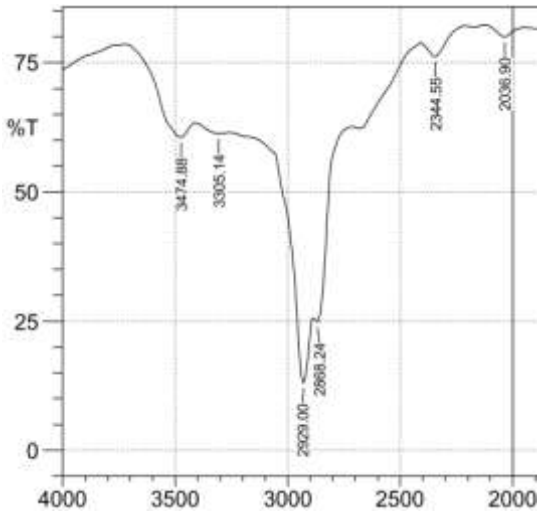


Fig. 1:FTIR spectrum of TCK oil

3.5 Effects of Process Variables on TC Kernel Oil Yield

3.5.1 Effect of time

The oil yield from soxhlet extractor operated at maximum time of 150 min are presented in Fig. 2(a andb) for hexane and petroleum ether, respectively. As time increased from 30 to 150 min,average oil yield increased from 31.84 to 48.39 %and 29.10 to 43.37 %, for hexane and ether, respectively. Also, as particle sizes decreased (considering same time range) from 2.5 to 0.5 mm, average oil yield increased from 38.22 to 50.01 %and 33.65 to 46.97 % , for hexane and ether, respectively.Fig. 2 indicated that extraction rate was fast initially and gradually decreased. This was due to the high rate of dissolution of free oil from the surface of TCK when exposed to the fresh solvent.Fig. 2 obviously indicates that higher oil yield was obtained using n-hexane. Hence, n-hexane waspreferred to ether as solvent in this report (Agu 2014). These solvents performances in this report were in agreement with the works of sayyar et al., (2009) and Sulaiman et al., (2013) for the extraction of jatropha seeds oil and solid coconut waste oil, respectively.

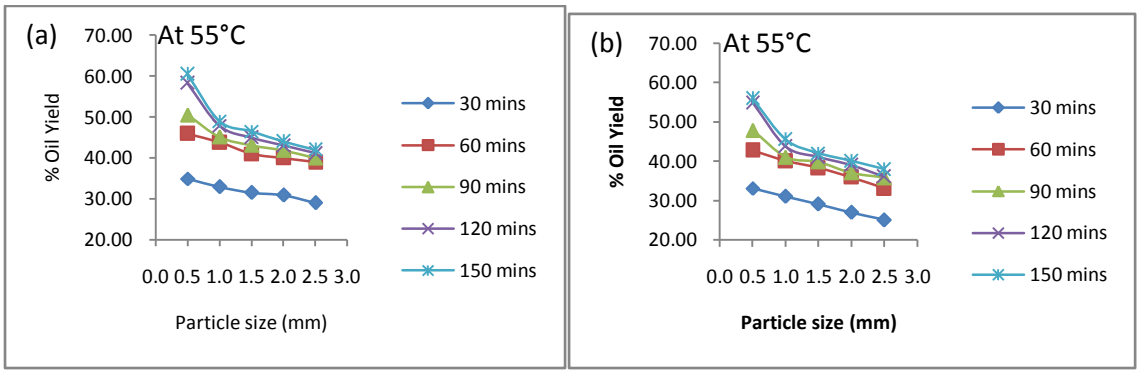


Fig. 2 a & b: Temporal variation of time on yield at 55°C for n-hexane and petroluem ether, respectively.

3.5.2 Effect of particle size

The oil yield generally increased as the particle size decreased (Figs. 3a and b).This was in line with the works of Sulaiman et al., (2013) andSirisompong et al., (2011) for the extraction ofsolid coconut waste oil and *Nepheliumlappaceum L.*, respectively. The particle sizes considered were 0.5, 1.0, 1.5, 2.0and 2.5mm. Their corresponding oil yields (at 55°C and 150min) were 60.45, 49.00, 46.50, 44.00, 42.00 and 56, 45.60, 42.11, 40.12, 38.01% for hexane and ether, respectively. Highest oil yield was obtained with the smallest particle size (0.5mm) and least with the highest particle size (2.5mm)for both solvents. N-hexanehad betterperformance irrespective of the particle size. These findings were in line with those reported by Huang et al., (2011) and Sulaiman et al., (2013).

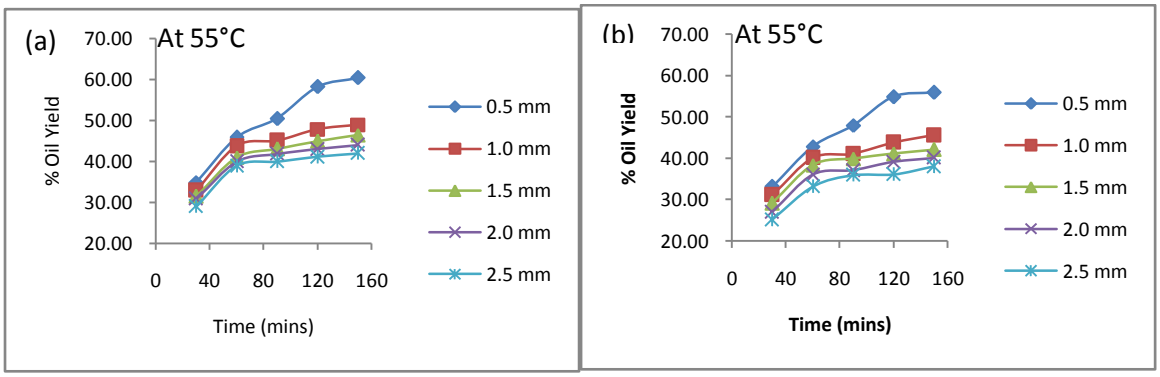


Fig. 3 a & b: Effects of particle sizes on yield at 55°C studied at different times for n-hexane and petroluem ether, respectively.

3.5.3 Effect of temperature

The influence of temperature on oil yield was examined at 35, 40, 45, 50 and 55°C for constant particle size of 0.5mmwithin 30 to 150 min as shown in Fig. 4(a andb,).As both temperature (35 to 55°C) and time (30 to 150 min) increased, the oil yield generally increased due to the increase in diffusion of oil as the oil viscosity decreased with temperatures increase (Sulaiman et al., 2013; Eikani et al., 2012). Also, the mass transfer

coefficient of the process increased with temperature rise (Sulaiman et al., 2013). Irrespective of the temperature, higher oil yield was obtained using n-hexane.

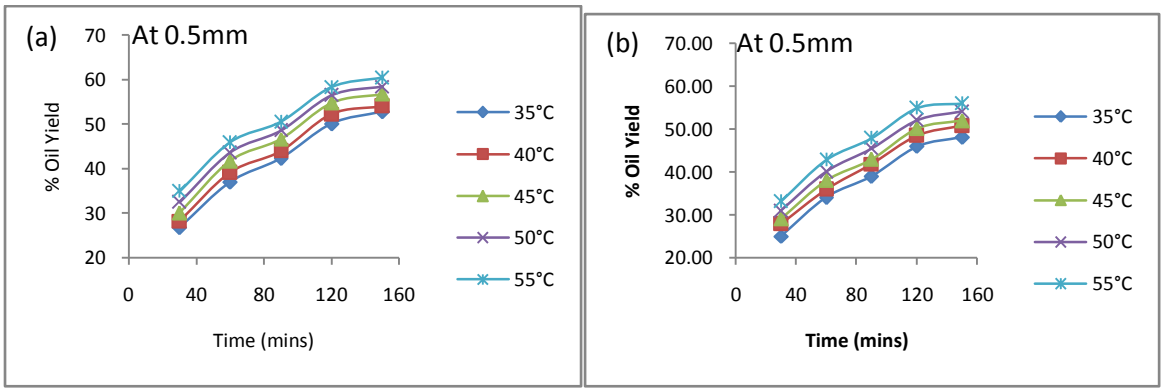


Fig. 4 a & b: Effect of temperature on yield at 0.5 mm studied at different time for n-hexane and petroluem ether respectively.

3.6 Kinetics parameters of TCK oil extraction

Tables 4 and 5 show kinetic parameters for TC kernel oil extraction using n-hexane and petroluem ether, respectively. The hyperbolic and Pseudo second order models kinetic parameters and theirrespective calculated oil yields obtained at different operating conditions were calculated using Equations in Table 1. The kinetic parameters for hyperbolic and Pseudo second order models were obtained from the plots of $1/\overline{y}$ against 1/t and t/C_t verses t, respectively. Furthermore, their calculated oil yields were obtained by substituting the obtained kinetic parameters into equations for hyperbolic and Pseudo second order models, respectively.

From the data in Tables 4 and 5, it was evident that the kinetic parameters C_s and C_1 for Pseudo second order and hyperbolic models, respectively, increased with increase in temperature. Thus, the reason for the increase in the oil yield as temperature increased. This increase in oil yield with temperature was due to the thermodynamic effect of oil solubilization inside the solid kernel particles (Liauw et al., 2008). Similarly, the parameter C_s in Pseudo second order models for both solvents increased with smaller particle size diameter (Agu, 2014). On the other hand, kinetic parameters of K and C_2 did not have a definite trend as could be observed in Tables 4 and 5.

Furthermore, it was evident from Tables 4 and 5 that the values of the pseudo second order kinetic parameter C_s for the extraction using n-hexane were higher than those obtained using petroleum ether within the entire experimental conditions. Also, the average values of the kinetic parameter K at most temperatures considered were also higher in n-hexane when compared to petroleum ether. Similarly, the average values of the kinetic parameter C_1 for hyperbolic model obtained at the various temperatures were also higher in n-hexane, compared to petroleum ether.

As could be seen in Table 4, R^2 values of 0.9854 and 0.9995 were obtained for hyperbolic and pseudo second order models, respectively, at 0.5mm and 55°C using n-hexane. Similarly, the R^2 values of 0.9859 and 0.9948 were obtained for hyperbolic and pseudo second order models, respectively at 0.5 mm and 55°C using petroleum ether (Table 5).

3.7 Variation between experimental and calculated linear models oil yields

The calculated oil yields for the kinetic models (hyperbolic and pseudo second order) using equations in Table 1,are presented in Tables 4 and 5, for n-hexane and petroleum ether, respectively. Studies were carried out for each of the five different temperatures (35 °C, 40 °C, 45 °C, 50 °C and 55 °C) at five different average particles size diameters (0.5, 1.0, 1.5, 2.0 and 2.5 mm).

On close examination of the oil yield data values, it could be ascertained that the oil yields obtained from the linear models were generally close to that obtained from experiment, as would be later buttressed by statistical R^2, RMS and SD results presented in Tables 4 and 5, for n-hexane and petroleum ether, respectively. However, the calculated yields of hyperbolic and pseudo second order models were closer to the experimental yield.

For instance, the highest calculated oil yields of 58.84 % and 60.08 % were obtained for hyperbolic and pseudo second order models, respectively, at 55 °C, 0.5 mm and 150 min, using n-hexane. These values were relatively close to the TCK oil yield (60.45 %) obtained experimentally under the same conditions. This therefore shows that both models fit the extraction of oil from TC kernel using n-hexane. On the other hand, the highest

calculated oil yields of 55.01 % and 56.20 % were obtained for hyperbolic and pseudo second order models, respectively, at 55 °C, 0.5 mm and 150 min, using petroleum ether. These values were close to TCK oil yield (56.00 %) obtained experimentally at the same conditions. Therefore, these models fit the extraction of oil from TC kernel using petroleum ether (Agu, 2014).

However, it was observed that higher oil yield of TC kernel was obtained using n-hexane when compared to petroluem ether. This was because hexane (0.0 polarity index) is greatly more non-polar when compared to petroluem ether (0.1 polarity index) (HPLC solvent Guide, 2002). This therefore facilitated easier penetration of hexane into the matrix of the TC kernel particles (Agu, 2014; Sulaiman et al., 2014).

In other words, variation in particle size, extraction time and temperature influenced the oil yield of TCK significantly irrespective of the solvent used. Furthermore, solvent type also influenced the oil yield of TCK (Agu, 2014; Sulaiman et al., 2014; Kostic et al., 2014).

3.8 Statistical comparison of kinetic models using error analysis

Linear coefficient of determination (R^2), root mean square (RMS), and standard deviation (SD) were used to evaluate how well the studied models represent the experimental data and to choose the best model. Tables 4 and 5 summarizes the percentage average values of the RMS, SD and the linear correlation coefficient for each model for the extraction using n-hexane and petroleum ether, respectively. From Tables 4 and 5, it was evident that irrespective of the particle size used, the individual values of the average RMS were less than ± 5% for each of the two models studied. Similarly, Tables 4 and 5 show the values of the SD for each kinetic model and for all extraction conditions carried out using n-hexane and petroleum ether, respectively. From Tables 4 and 5,it was also obvious that regardless of the particle size used, individual values of the average SD were less than 0.01 for each of the two models studied. Therefore, on the bases of their low RMS and SD, the models examined reasonably described the kinetics of oil extraction from TCK. These results were in line with that obtained by Kitanovic et al. (2008) for the extraction of resinoid from aerial parts of *HyperiumPerforatum L.*From theresults in Tables Tables 4 and 5, it could be seen that in most cases, irrespective of the solvent used in the extraction process, the least values of the RMS and SD for the models were obtained at the highest extraction temperature of 55 °C and smallest particle size of 0.5mm, thus confirming significant correlation of temperature and particle size with related models irrespective of the kinetic model used (Seikova et al., 1999; Agu 2014).

Tables 4 and 5 show that while the average RMS and SD decreased, the best fit of the models increased in the order shown below, irrespective of the solvent used in the extraction process:
Hyperbolic Model → Pseudo second order.

Similarly, the average linear correlation coefficient R^2 value increased in the following order;
Hyperbolic Model → Pseudo second order

On the basis of the obtained results, Pseudo second order, having the highest value of the R^2, and lowest RMS and SD values was chosen as the better extraction kinetics model when compared to hyperbolic model.

3.9 Thermodynamic parameters

Table 6 shows the values of equilibrium constants and other thermodynamic parameters for oil extraction using n-hexane and petroleum ether. Figs.5 a and b show the plots of In K vs. 1/T for particle sizes 0.5 to 2.5mm, which were used to determine the values of the thermodynamic parameters. The enthalpy values for n-hexane were in the range of 182.81 – 598.74KJ/mol for the different particle sizes (Menkiti et al., 2015). However, the enthalpies for petroleum ether were in the range of 195.18 – 402.67KJ/mol. Theenthalpies increased with increase in the particle size for the n-hexane. Similarly, in the case of petroleum ether, theirenthalpies increased with increase in particle size,except in few cases. This was due to more energy required to extract oil from larger seed particles than from smaller ones. The values of the enthalpies in this report were comparatively higher than those of melon and rubber seed oilsreported byIbemesi and Attah (1990),coconut by Sulaiman et al. (2013), and olive cake oil by Meziane and Kadi (2008). This could be attributed to the morphology of the seed which could influence oil extraction (Menkiti et al., 2015; Agu, 2014). The positive enthalpy change showed that the extraction process was endothermic in nature, thus, required external source of energy during the process (Sulaiman et al., 2013; Amin et al., 2010; Topallar, 2000).

The positive values of entropy change for the entire process irrespective of the solvent used was an indication that the process was irreversible, thus in agreement with the findings of Sulaiman et al., (2013), Amin et al., (2010), Meziane and Kadi (2008) and Topallar (2000). The entropy values for the extractions using n-hexane and petroleum ether were between 0.643 – 2.04 KJ/mol and 0.686 – 1.44, respectively. These higher entropy

values recorded for n-hexane, compared to that of petroleum ether could be attributed to the higher oil yield obtained with n-hexane. This is because entropy of a mixture increases with increase in the number of molecules which is often associated with increase in oil yield (Agu, 2014).

Furthermore, the free energy values for both extractions with n-hexane and petroleum ether were all negative. This was an indication that the processes were feasible and spontaneous. The negative values of the free energy for both n-hexane and petroleum ether were an indication that the processes were spontaneous. Finally, from the thermodynamic study, it was clear that energy needed to break the solute-solute as well as the solvent-solvent interactions was lesser than the energy given up in solute-solvent interaction (Menkiti et al., 2015; Sulaiman et al., 2013).

Table 4: Kinetic parameters for TC kernel oil extraction at 35, 40, 45, 50 and 55°C using n-hexane

	35°C					40°C					45°C					50°C					55°C				
	0.5mm	1.0mm	1.5mm	2.0mm	2.5mm	0.5mm	1.0mm	1.5mm	2.0mm	2.5mm	0.5mm	1.0mm	1.5mm	2.0mm	2.5mm	0.5mm	1.0mm	1.5mm	2.0mm	2.5mm	0.5mm	1.0mm	1.5mm	2.0mm	2.5mm
Hyperbolic																									
C_1 (min^{-1})	1.47	1.69	1.61	1.57	1.27	1.59	1.88	1.76	1.70	1.49	1.72	2.14	2.20	2.18	1.75	1.97	2.41	2.30	2.39	2.14	2.23	2.67	2.63	2.76	2.49
C_2 (min^{-1})	0.0221	0.0336	0.0342	0.0354	0.0289	0.0233	0.0359	0.0361	0.0364	0.0326	0.0241	0.0402	0.0446	0.0470	0.0372	0.0278	0.0446	0.0442	0.0493	0.0453	0.0313	0.0476	0.0495	0.0550	0.0510
$\bar{\bar{y}}$ (wt.%)	51.20	41.92	39.48	37.39	35.79	52.92	44.16	41.18	39.50	37.90	55.95	45.62	42.86	40.73	39.81	57.19	47.03	45.25	42.76	41.12	58.84	49.56	46.85	44.78	43.15
R^2	0.9880	0.9822	0.9860	0.9628	0.9570	0.9888	0.9767	0.9719	0.9653	0.9598	0.9909	0.9880	0.9749	0.9585	0.9726	0.9888	0.9751	0.9887	0.9734	0.9782	0.9854	0.9788	0.9772	0.9791	0.9584
RMS (%)	3.238	2.621	2.312	3.701	4.122	3.053	2.868	3.144	3.481	4.135	2.693	1.890	2.560	3.171	3.044	2.767	2.561	1.734	2.432	2.379	2.832	2.225	1.553	1.994	3.006
SD (%)	0.017	0.008	0.479	0.508	0.495	0.334	0.574	0.185	0.090	0.262	0.537	0.378	0.318	0.234	0.164	0.229	0.462	0.465	0.211	0.616	0.457	0.131	0.287	0.316	0.585
2nd order																									
C_s	70.92	48.31	45.45	42.02	40.65	71.43	50.25	46.51	44.64	42.55	74.07	52.08	47.62	44.83	44.84	74.63	51.81	51.02	47.17	45.25	75.19	55.25	52.08	48.54	46.51
K	**$2.6x10^{-4}$**	**$8.1x10^{-3}$**	**$8.7x10^{-4}$**	**$1.1x10^{-3}$**	**$9.5x10^{-4}$**	**$2.9x10^{-4}$**	**$8.4x10^{-4}$**	**$9.6x10^{-4}$**	**$9.9x10^{-3}$**	**$1.0x10^{-3}$**	**$2.9x10^{-4}$**	**$8.4x10^{-4}$**	**$1.1x10^{-3}$**	**$1.3x10^{-3}$**	**$1.0x10^{-3}$**	**$3.2x10^{-4}$**	**$1.1x10^{-3}$**	**$9.6x10^{-4}$**	**$1.2x10^{-3}$**	**$1.2x10^{-3}$**	**$3.5x10^{-4}$**	**$9.7x10^{-4}$**	**$1.0x10^{-3}$**	**$1.4x10^{-3}$**	**$1.4x10^{-3}$**
c_t (wt.%)	52.24	41.27	38.89	36.53	34.64	53.85	43.41	40.44	38.81	36.84	56.59	45.22	42.27	40.14	39.10	58.41	46.20	44.85	42.20	40.34	60.08	49.05	46.36	44.05	42.22
R^2	0.9899	0.9976	0.9976	0.9955	0.9934	0.9980	0.9973	0.9967	0.9960	0.9938	0.9989	0.9987	0.9978	0.9970	0.9970	0.9990	0.9979	0.9989	0.9982	0.9983	0.9995	0.9984	0.9993	0.9989	0.9975
RMS (%)	3.421	2.886	2.577	4.137	4.822	3.194	3.142	3.606	3.838	4.783	2.832	1.993	2.893	3.514	3.464	2.992	3.077	1.852	2.634	2.806	3.110	2.384	1.671	2.379	3.582
SD (%)	0.796	0.743	0.907	1.328	1.394	0.647	1.126	1.275	1.294	1.635	0.470	0.666	0.567	0.937	0.984	0.081	1.372	0.733	0.391	0.696	0.500	0.179	0.139	0.112	1.075

Table 5: Kinetic parameters for TC kernel oil extraction at 35, 40, 45, 50 and 55°C using petroleum ether

	35°C					40°C					45°C					50°C					55°C				
	0.5mm	1.0mm	1.5mm	2.0mm	2.5mm	0.5mm	1.0mm	1.5mm	2.0mm	2.5mm	0.5mm	1.0mm	1.5mm	2.0mm	2.5mm	0.5mm	1.0mm	1.5mm	2.0mm	2.5mm	0.5mm	1.0mm	1.5mm	2.0mm	2.5mm
Hyperbolic																									
C_1 (min^{-1})	1.41	1.67	1.65	1.32	1.17	1.67	1.85	1.90	1.48	1.28	1.79	2.17	2.01	1.80	1.52	1.95	2.43	2.46	2.09	1.68	2.16	2.69	2.53	2.22	1.99
C_2 (min^{-1})	0.0235	0.0377	0.0408	0.0335	0.0315	0.0273	0.0399	0.0447	0.0353	0.0328	0.0289	0.0459	0.0446	0.0423	0.0376	0.0305	0.0492	0.0541	0.0472	0.0393	0.0327	0.0527	0.0523	0.0480	0.0453
$\bar{y}$ (wt.%)	46.65	37.60	34.66	32.96	30.57	49.01	39.67	36.88	35.19	32.46	50.42	41.38	39.19	36.76	34.39	52.59	43.39	40.47	38.77	36.69	55.01	45.30	42.85	40.65	38.40
R^2	0.9870	0.9741	0.9803	0.9542	0.9784	0.9768	0.9844	0.9706	0.9664	0.9835	0.9812	0.9671	0.9788	0.9553	0.9755	0.9839	0.9708	0.9676	0.9699	0.9907	0.9859	0.9819	0.9741	0.9770	0.9844
RMS (%)	3.208	2.926	2.402	4.266	3.161	3.691	2.179	2.770	3.559	2.644	3.312	2.943	2.332	3.556	2.906	2.905	2.588	2.511	2.683	1.759	2.625	1.945	2.305	2.301	2.084
SD (%)	0.502	0.597	0.250	0.288	0.345	0.135	0.036	0.516	0.464	0.093	0.371	0.204	0.143	0.192	0.343	0.368	0.587	0.143	0.056	0.542	0.531	0.107	0.062	0.095	0.476
2nd order																									
C_s	64.10	42.74	39.53	37.31	35.34	65.79	45.45	40.65	39.37	37.59	66.23	46.95	43.67	40.82	39.06	68.03	48.31	44.25	43.29	42.19	69.44	51.02	46.73	45.05	42.74
K	$3.1x10^{-4}$	$1.0x10^{-3}$	$1.1x10^{-3}$	$1.1x10^{-3}$	$1.1x10^{-3}$	$3.3x10^{-4}$	$9.4x10^{-3}$	$1.3x10^{-3}$	$1.2x10^{-3}$	$1.0x10^{-3}$	$3.6x10^{-4}$	$1.0x10^{-3}$	$1.2x10^{-3}$	$1.3x10^{-3}$	$1.1x10^{-3}$	$3.7x10^{-4}$	$1.1x10^{-3}$	$1.1x10^{-3}$	$1.1x10^{-3}$	$9.9x10^{-4}$	$4.1x10^{-4}$	$1.0x10^{-3}$	$1.4x10^{-3}$	$1.2x10^{-3}$	$1.2x10^{-3}$
c_t (wt.%)	47.89	37.01	34.36	32.17	29.96	50.42	39.34	36.17	34.31	31.97	51.69	41.20	38.70	36.14	33.84	54.41	42.97	39.99	38.39	36.41	56.20	45.34	42.25	40.16	37.86
R^2	0.9907	0.9969	0.9977	0.9938	0.9948	0.9909	0.9981	0.9978	0.9958	0.9966	0.9915	0.9954	0.9982	0.9961	0.9962	0.9942	0.9975	0.9981	0.9974	0.9982	0.9948	0.9981	0.9985	0.9984	0.9979
RMS (%)	3.404	3.055	2.452	4.595	3.379	3.952	2.221	3.105	4.109	2.841	3.600	2.930	2.634	3.884	3.046	3.342	2.626	2.711	2.764	1.797	2.826	1.945	2.730	2.508	2.304
SD (%)	0.283	0.382	0.404	0.824	0.355	0.581	0.077	0.417	1.389	0.684	0.622	0.195	0.673	0.883	0.171	1.965	0.228	0.204	0.145	0.472	0.063	0.360	0.918	0.470	0.441

Table 6. Thermodynamic parameters for the extraction of TC kernel oil using n-hexane and petroleum ether.

T	0.5mm				1.0mm				1.5mm				2.0mm				2.5mm			
(K)	K	ΔH KJ/mol	ΔS KJ/mol	ΔG KJ/mol	K	ΔH KJ/mol	ΔS KJ/mol	ΔG KJ/mol	K	ΔH KJ/mol	ΔS KJ/mol	ΔG KJ/mol	K	ΔH KJ/mol	ΔS KJ/mol	ΔG KJ/mol	K	ΔH KJ/mol	ΔS KJ/mol	ΔG KJ/mol
N-hexane																				
308	4.73×10^{2}			-15.77	3.31×10^{6}			-38.44	1.95×10^{6}			-37.09	8.44×10^{6}			-40.84	5.43×10^{5}			-33.81
313	1.11×10^{3}			-18.24	1.14×10^{7}			-42.28	1.50×10^{7}			-43.00	1.43×10^{7}			-42.87	9.39×10^{6}			-41.16
318	2.51×10^{3}	182.81	0.643	-20.69	5.02×10^{7}	344.89	1.24	-46.88	5.83×10^{8}	334.95	1.34	-53.36	1.80×10^{9}	503.39	1.76	-56.35	2.21×10^{7}	598.74	2.04	-44.70
323	9.37×10^{3}			-24.56	4.88×10^{9}			-59.91	1.15×10^{9}			-56.02	5.83×10^{9}			-60.38	3.78×10^{9}			-59.22
328	3.81×10^{4}			-28.76	4.62×10^{9}			-60.68	1.62×10^{10}			-64.11	1.42×10^{12}			-76.30	1.44×10^{12}			-76.34
Pet. Ether																				
308	5.95×10^{2}			-16.36	8.30×10^{6}			-40.80	1.02×10^{7}			-41.34	5.32×10^{5}			-33.76	5.41×10^{5}			-33.80
313	1.90×10^{3}			-19.65	1.68×10^{7}			-43.29	4.16×10^{8}			-51.64	8.12×10^{6}			-41.40	9.32×10^{5}			-35.77
318	4.51×10^{3}	195.18	0.686	-22.25	3.89×10^{8}	308.35	1.13	-52.29	1.36×10^{8}	402.67	1.44	-49.52	7.67×10^{7}	345.55	1.23	-48.00	1.14×10^{7}	336.87	1.20	-42.97
323	1.56×10^{4}			-25.93	1.54×10^{9}			-56.80	3.39×10^{10}			-65.11	4.85×10^{8}			-53.71	1.83×10^{7}			-44.90
328	6.98×10^{4}			-30.42	8.44×10^{9}			-62.33	1.86×10^{10}			-70.77	1.97×10^{9}			-58.37	2.93×10^{9}			-59.44

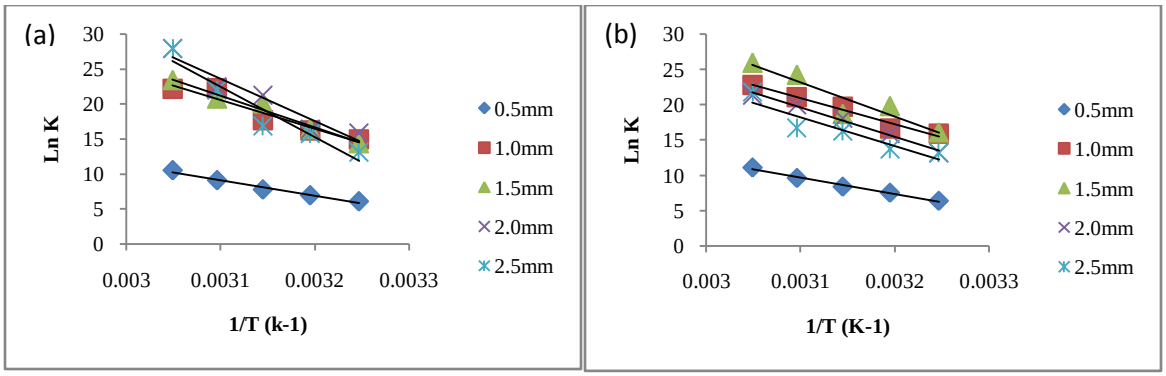


Fig. 5 a & b: Plot of In K (equilibrium constant) vs. 1/T (temperature, K) for the five different particle sizes for n-hexane and petroluem ether respectively.

4.0. Conclusion

In this study, n-hexane was found to be the better solvent for TC kernel oil extraction since it gave the higher oil yield compared to petrolum ether. Process parameters of temperature, particle size and time influenced the oil yield in both solvents. Highest TC kernel oil yields of 60.45% and 56% were obtained using n-hexane and petrolume ether, respectively, at 55°C, 0.5 mm and 150 min. Physicochemical properties of the extracted TC kernel oil indicates its potential used as transformer fluid upon further purification, while the fatty acid composition indicated that it was highly unsaturated. For both solvents, pseudo second order and hyperbolic models reasonably described the process kinetics as indicated by their high R^2 and low RMS and SD values. However, pseudo second order model gave the better fit in both cases. The ΔG, ΔS and ΔH values obtained at the five different particle sizes used during the extraction for bothsolvents indicated that the extraction process was spontaneous, irreversible, and endothermic, with n-hexane having higher average values of ΔH and ΔS. Thus justifies the reason for the high oil yield obtained using n-hexane.

5.0 Recommendation

N-hexane is recommended for solvent extraction of oil from TC kernel and other seed/nuts oil extraction since it gave the higher oil yield compared to petrolum ether. Furthermore, TC kernel oil is recommended for use as transformer fluid upon further purification. For the extraction kinetics modeling, psudo second order model is recommended because it gave the best fit to extraction kinetics data.

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Acknowledgements

The authors wish to thank the staff of Transmission Company of Nigeria (TCN) Enugu Regional office and Onitsha sub-region for opportunity to carry out the dielectric strength analysis of the oil and other analyses tests using the machines in their laboratory. In a special way we thank Engr. Jack Emuche, the Assistant General Manager for giving instant approval for these analyses to be done without delay.