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Kinetics and thermodynamic studies on *Moringa oleifera* oil extraction for biodiesel production via transesterification

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ABSTRACT

Moringa oleifera produces oil which can be extracted and converted to biodiesel. However, the kinetics and thermodynamics of this viable fuel have been seldomly investigated. We examine the kinetics and thermodynamics of the oil extraction for biodiesel production. The biodiesel kinematic viscosity ($3.75 \pm 0.04 \text{ mm}^2/\text{s}$), cetane number (67.12), oxidative stability (15.2 ± 0.5), acid value (0.012 mg/KOH), pour point (-9°C) and carbon residue (0.020 ± 0.001) satisfy the American Society for Testing and Materials (ASTM) limits. Fourier transform infrared spectroscopy distinguishes the biodiesel and the base oil at 1435.77 cm^{-1} ($-\text{CH}_3$ stretch), 1195.74 cm^{-1} ($\text{O}-\text{CH}_3$) and 1377.67 cm^{-1} ($\text{O}-\text{CH}_2$) because $-\text{CH}_3$ and $\text{O}-\text{CH}_3$ stretches are absent in the oil whereas the biodiesel lacks $\text{O}-\text{CH}_2$ stretch. The highly negative activation entropy ($-214.11 \pm 0.16 \text{ J mol}^{-1} \text{ K}^{-1}$) and greater activation enthalpy ($30.39 \pm 0.05 \text{ kJ/mol}$) indicate a slower extraction rate due to the higher energy requirement and stiffer transition of the extraction, respectively. The slower extraction rate agrees with the lower mass transfer coefficients ($0.0119\text{--}0.0210 \text{ min}^{-1}$). The equilibrium constant (K) is positive whilst the Gibbs free energy (ΔG) is negative, indicating a forward and spontaneous process. This investigation of kinetics, thermodynamics and transesterification essentially provides in-depth knowledge on oil extraction and biodiesel production.

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Introduction

The global energy crisis arising from the consumption of fossil fuels is a major concern in many countries, due to the fast depletion of fossil feed stocks, increasing fuel prices and increasing $\text{CO}_{2(g)}$ emissions which result in global warming [1]. Therefore, the world needs to move from the consumption of fossil fuels to renewable or alternative sources of energy such as biofuels and biodegradable fuels. Alternative or renewable energy sources release less $\text{CO}_{2(g)}$ [2–5]. The most explored of these energy sources are biodiesel and bioethanol [5–8].

The vast availability of raw materials, renewability, biodegradability and lower $\text{CO}_{2(g)}$ emissions make biodiesel superior to other energy sources [1,3,4,8]. Biodiesel fuel will help develop the agriculture industry of countries that use it significantly and consistently [9]. Some of the raw materials studied are green microalgae, and seeds and other parts of plants [2,7]. Several methods are used to extract bio-oil from these raw materials, which is then converted to biodiesel [11–13]. Ethers, esters, hexane, butanol and ethanol and their respective combinations are superior solvents for the extraction [14,15].

Mostly, transesterification converts the crude oil into biodiesel. For example, transesterification is used to convert conventional sources, including palm oil [16], groundnut oil [17], *Jatropha curcas* oil [18], palm kernel oil [19] and shea butter [20], to biodiesel. However, conventional biodiesel sources have associated drawbacks. Biodiesel from conventional sources has created a strain on food production, price and availability [21]. As a result, we need to widely explore unconventional biodiesel

sources. Moringaceae is a prominent unconventional biodiesel source suitable for extensive study. Moringaceae is a family of oilseed trees, with a single genus and 14 species. In this family, *Moringa oleifera*, common in Africa, India, South East Asia, Arabia, the Caribbean Islands, the Pacific, Pakistan, and South America, is predominant [22,23]. Information on annual production of moringa seed and oil is scarce. Some studies have reported 1.1–1.3 million tons/380 km² annual fruit production in India [24,25], whereas another reported 16.74 tons/hectare average seed production in Nigeria between 2007 and 2009 [26]. The oil content accounts for 36.7% of the seed dry weight [27]. *Moringa oleifera* is a fast-growing plant, tolerant to drought, poor soil and a pH range of 5.0–9.0 [28]. The edibility of moringa oil is not well established scientifically; Alessandro *et al.* mentioned its potential edibility due to its nutritional value [27]. Nevertheless, the major interest is currently in biodiesel production due to its high biodiesel production potential: it has high oleic acid (>70%), high resistance to oxidation, high thermal stability ($425\text{--}450^\circ\text{C}$) and a high cetane number (CN; 67) [24,29–33].

Despite the promising characteristics of *Moringa oleifera* oil, few studies have been conducted on the extraction and characterization of oil from *Moringa oleifera*. Furthermore, information on the kinetics and thermodynamics of extracting the oil for biodiesel production is limited.

Therefore, we examine the kinetics and thermodynamics (enthalpy change, entropy change, Gibbs free energy) of the extraction of *Moringa oleifera* oil for biodiesel production via transesterification. The physico-chemical characteristics of the crude *Moringa* oil and its biodiesel are investigated and presented.

Materials and methods

Seed preparation

The *Moringa* seeds were removed from the fruits and the testa from the seeds. The seeds were oven dried at 60°C to a constant weight, and a kitchen grinder was used to grind the dried seed to a mesh size of No. 120 [34].

Solvent extraction, chemical kinetics and thermodynamics

Solvent extraction is an effective method for use with *Moringa* oil [33]. Therefore, we adopted the experimental set-up of Amin *et al.* and used n-hexane to extract the oil. The set-up included a three-necked round-bottom flask, condenser, sampler, thermometer, and water bath with magnetic stirrer [35].

In the preliminary studies, the optimum powdered seed weight (g) to solvent volume (mL) ratio was 1:10. In the set-up, 200 mL of hexane continually extracted the oil from 20 g of *Moringa* powder at 50°C within 50–130 min at 20-min interval (Figure 1). We measured the first extract at 50 min because the quantity of oil produced before 50 min was too small to quantify gravimetrically.

Within the same period and interval, the extraction was repeated at 55, 60 and 65°C. The physico-chemical parameters were measured while Fourier transform infrared

spectroscopy (FTIR) was used to identify the functional groups in the crude oil and the biodiesel.

Transesterification of the crude *Moringa oleifera* oil

Prior to the transesterification process, the *Moringa* oil was treated using the procedure of Canakci and Van Gerpen since the acid value was high (2.84) [36]. The transesterification and biodiesel treatment were partly adapted from the approach of Rashid *et al.* [30]. In our study, 1 wt. % KOCH₃ catalyst was used to transesterify the oil to biodiesel (Figure 2).

Fatty acid profile and oxidative stability of the biodiesel

We followed the European method, EN14103:2011 (using the methyl nonadecanoate internal standard) to determine the fatty acid profile of the biodiesel. An Agilent 7890 A (Agilent Technologies, USA) gas chromatograph (GC) with HP INNOWax column (30 m × 25 mm × 25 μm) was used to determine the fatty acid methyl ester (FAME) contents of the biodiesel. It was equipped with an Agilent 7693 Autoinjector (1 μL injection volume) and a flame ionization detector (FID), both operated at 250°C. Helium was used as the carrier gas, set at a flow rate of 1 mL/min. At an initial oven temperature of 100°C which was kept constant for 15 min then raised to 240°C at 5°C/min, the GC separated

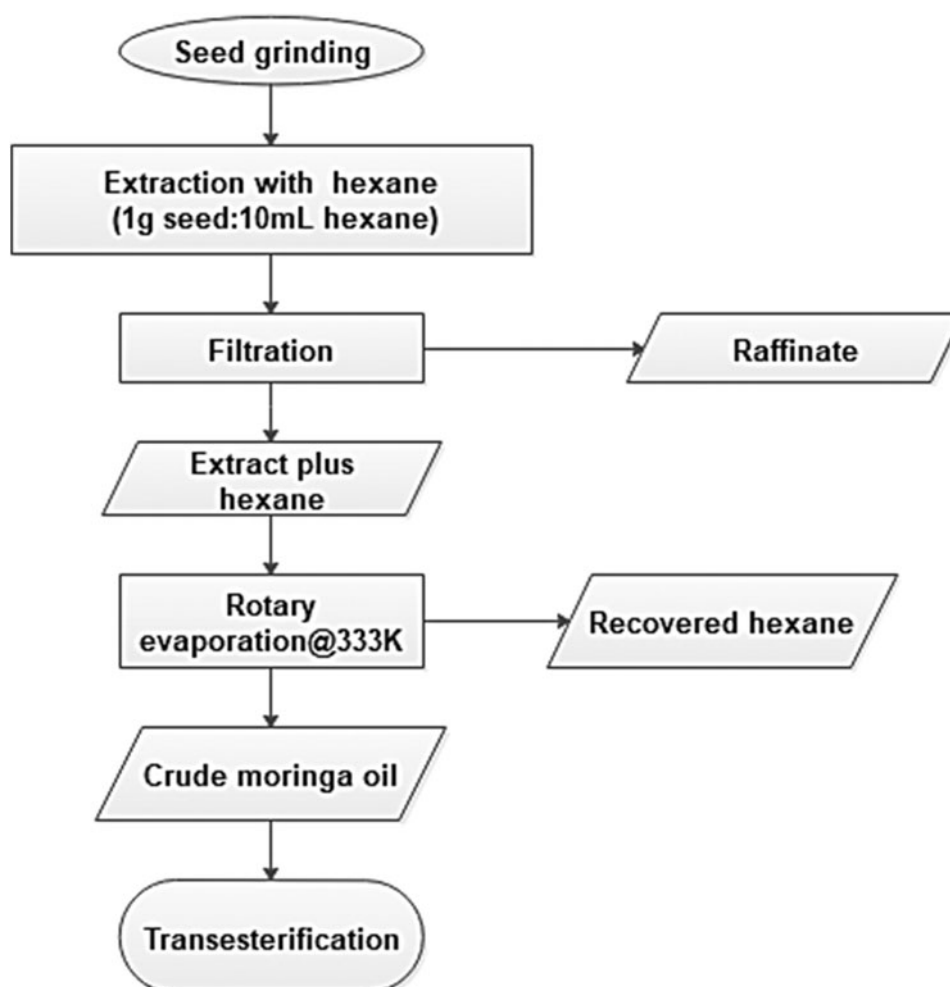


Figure 1. Simplified flow chart for *Moringa* oil extraction followed by transesterification.



Figure 2. Photograph of Moringa biodiesel.

the FAMES. The retention time and peak area represented the respective fractions of the fatty acids.

The Rancimat instrument (Metrohm, model 743, Switzerland) was used to determine the oxidative stability (OS) of the biodiesel [37]. Five grams of the biodiesel was oxidized in a reaction tube at 110°C under air (flow rate 20 L/h) which carried the volatile oxidation products to the conductometric cell, pre-filled with 60 mL of distilled water. The conductometric cell constantly measured the electrical conductivity of the distilled water. The OS was expressed as the induction point, IP (h). At IP, the water conductivity increases over time due to the fatty acid oxidation.

All reproducible measurements were triplicated. Any measurements without uncertainty values are averages of duplicate points. Microsoft Excel 2016 was used for all graphs and calculations.

Determination of physico-chemical properties of Moringa oleifera oil

Following the American Society for Testing and Materials standard ASTM D6890, and the method of Knothe *et al.*, an ignition quality tester was used to determine the CN [38]. Adhering to ASTM D97-12, a pour point analyzer with temperature reading +20°C to -80°C was used to measure the pour point [39]. HV M472 multi-range viscometer tubes in Koehler Scientific Viscometer baths were used to determine the kinematic viscosity, applying ASTM D 445-97 [40]. The Cleveland Open Cup (COC) method (ASTM D92-12b) was applied [41], and the acid value was measured according to ASTM D664 [42].

Results and discussion

Fatty acid composition of Moringa oleifera oil

The study investigated the kinetics and thermodynamics of Moringa oil. The qualities of the oil relevant for biodiesel production are shown. Moringa oleifera biodiesel contains

Table 1. Fatty acid composition of Moringa oleifera biodiesel.

Fatty acid methyl ester		% Mole fraction
Palmitic	C16:0	6.1 ± 0.2
Palmitoleic	C16:1	1.2 ± 0.1
Stearic	C18:0	3.4 ± 0.2
Oleic	C18:1	79.3 ± 0.3
Linoleic	C18:2	1.4 ± 0.1
Linolenic	C18:3	1.1 ± 0.1
Arachidic	C20:0	2.1 ± 0.3
Behenic	C22:0	2.2 ± 0.1
Lignoceric	C24:0	3.2 ± 0.2

79% oleic acid and is a monounsaturated fatty acid (Table 1), whereas 17% is attributed to C16:0, C18:0, C20:0, C22:0 and C24:0.

FTIR analysis of Moringa oleifera oil and biodiesel

Generally, the peaks of the C-H and C=O functional groups in the Moringa oleifera oil are similar to those of the biodiesel at 3004.45–1742.23 cm⁻¹ (Figure 3).

The -CH bond occurs at 3004.45 cm⁻¹ (with -CH rocking at 721.94 cm⁻¹) in Moringa oil and 3004.08 cm⁻¹ (with -CH rocking at 722.18 cm⁻¹) in Moringa biodiesel; -CH₂ bonds are present at 2853.26–2922.40 cm⁻¹ in the oil and 2853.57–2922.56 cm⁻¹ in the biodiesel; -C=O bond stretch is distinct at 1744.27 cm⁻¹ in the oil and 1742.23 cm⁻¹ in the biodiesel [43].

However, the 'fingerprint' region at 1600–800 cm⁻¹ differentiates the triglycerides from the biodiesel. The biodiesel shows asymmetric stretching of -CH₃ at 1435.77 cm⁻¹ but this is absent in the oil [43]. In contrast, biodiesel lacks the glycerol group O-CH₂ (mono-, di- and triglycerides) but the oil spectrum portrays the O-CH₂ at 1377.67 cm⁻¹ [44]. The O-CH₃ stretch at 1195.74 cm⁻¹ is characteristic of biodiesel [45].

Physico-chemical properties of Moringa oleifera oil

The acid value, carbon residue and kinematic viscosity are improved by 99.5%, 99% and 84%, respectively, after transesterification, compared with the crude oil (Table 2). The biodiesel CN and flash point are 42.8% and 58.4% higher, respectively, than the minimum value of ASTM D6751 [46]. The CN (67.12), flash point (206 °C) and kinematic viscosity (3.75 ± 0.04 mm²/s) indicate that the biodiesel can ignite suitably under compression, which is a key requirement for diesel engines.

The CN and kinetic viscosity of the biodiesel obtained are similar to the values (67.07 and 3.83 mm²/s) reported in the literature on Moringa oleifera oil [30]. The biodiesel will flow consistently at lower temperature regimes around -9°C since the pour point is -9°C. The appreciable physico-chemical properties of the biodiesel are potentially suitable for diesel engines.

Determination of Moringa oleifera oil yield and kinetic parameters

The extraction temperatures used were 323, 328, 333 and 338 K. Increasing temperature and time increases the yield (Table 3). The maximum yield (10.18%) was generated at 338 K and 130 min. At each temperature, the extraction

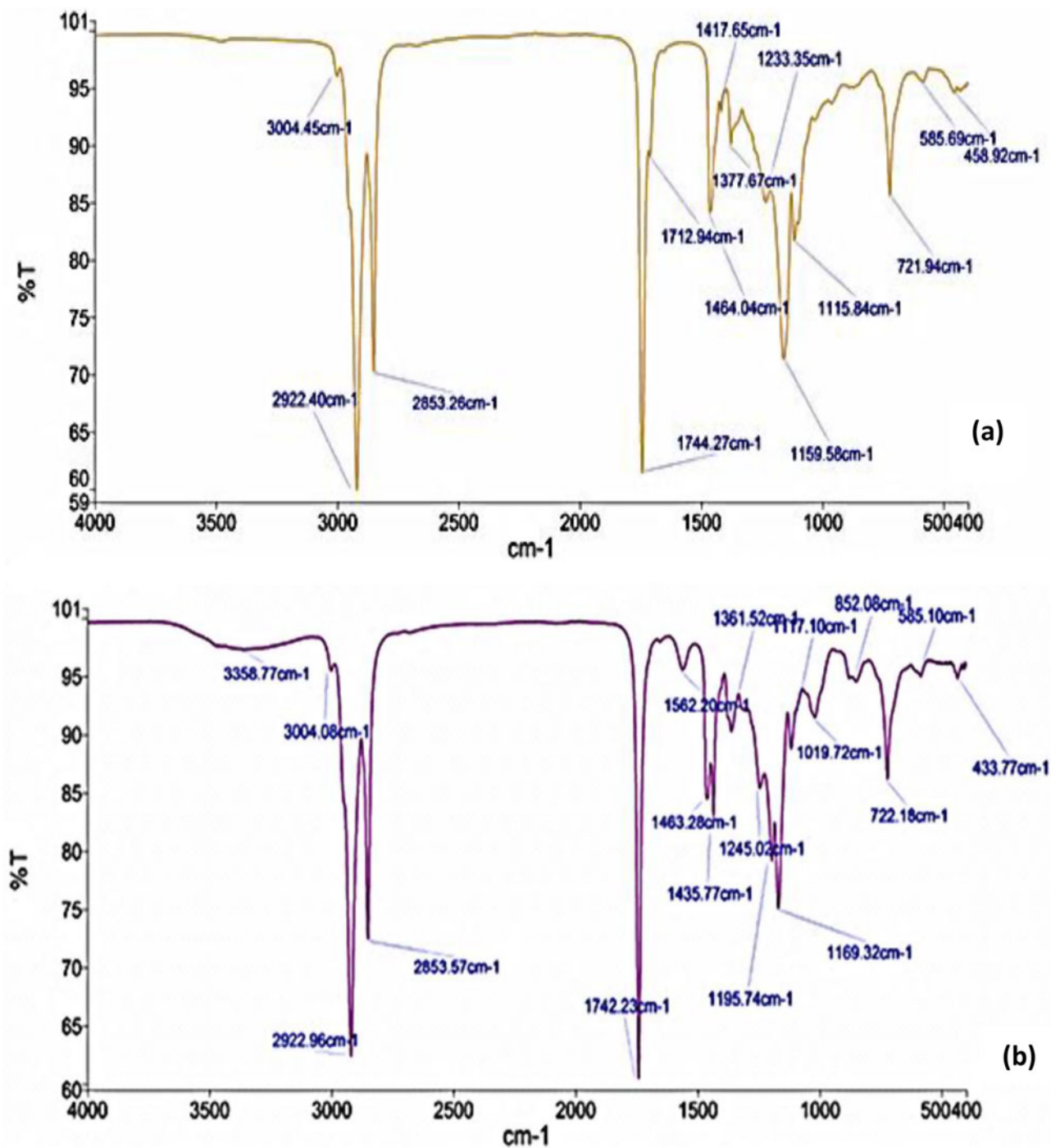


Figure 3. Comparison of the Fourier transform infrared spectra of (a) *Moringa oleifera* oil and (b) its biodiesel.

Table 2. Physico-chemical properties of the crude oil and its biodiesel compared to the American Society for Testing and Materials standard ASTM D6751.

Parameter	Moringa oil	Moringa biodiesel	ASTM D6751
Moisture content (%)	0.11 ± 0.08	0.21 ± 0.03	0.05 max
Acid value (mg KOH/g)	2.84	0.012	0.5 max
Carbon residue	2.07 ± 0.01	0.020 ± 0.001	0.05 max
Kinematic viscosity @ 40 °C (mm ² /s)	23.65 ± 0.1	3.75 ± 0.04	1.9–6.0
Cetane number (CN)	–	67.12	47 min
Oxidative stability (h) at 110 °C	–	15.2 ± 0.5	3 min.
Density(kg/m ³)	918	877.5	–
Flash point (°C)	–	206	130 min.
Pour point (°C)	–	–9	–
Refractive index n_D^{30}	1.462	1.454	–

rate equation follows Equation (1) [34,35].

$$\frac{dY}{dt} = k_r Y^n \quad (1)$$

where k_r = extraction constant; Y = percentage oil yield; n = reaction order; and t = extraction time.

Equation (1) can also be expressed as

$$\ln \frac{dY}{dt} = n \ln Y + \ln k_r \quad (2)$$

The plot of $\ln \frac{dY}{dt}$ versus $\ln Y$ produces a linear graph with n as the slope and $\ln k_r$ as the intercept.

Diffusive and convective mass transfer drive the oil extraction. Diffusion is dominant in the seed, whereas advection predominates in the solvent. However, mass transfer in the seed by diffusion is cumbersome to determine since the concentration gradient in the solid is unknown. Therefore, we represent the kinetic model of the oil extraction with convective transfer between the solid-liquid interphase where mass transfer by diffusion is equal to mass flow by convection, considering that a chemical reaction does not occur, and the process is non-steady state [44,47].

$$\frac{dC}{dt} = k \times (C_i - C_t) \quad (3)$$

Rearranging and integrating Equation (3), it becomes

$$-\ln \left(\frac{C_i - C_t}{C_i} \right) = kt \quad (4)$$

where C_i = mass concentration of oil at 130 min; C_t = mass concentration of extract at time t ; ($C_t=0$ at $t=0$), k = mass transfer coefficient

Table 3. Percentage oil yield at varying times and temperatures.

t (min)	Percentage oil yield (Y)			
	323 K	328 K	333 K	338 K
50	1.94 ± 0.01	3.49 ± 0.03	5.43 ± 0.02	6.82 ± 0.04
70	2.57 ± 0.02	4.32 ± 0.03	6.44 ± 0.02	7.61 ± 0.05
90	3.36 ± 0.04	5.27 ± 0.04	7.58 ± 0.05	8.43 ± 0.04
110	4.28 ± 0.05	6.36 ± 0.05	8.82 ± 0.06	9.29 ± 0.06
130	5.39 ± 0.05	7.56 ± 0.06	10.17 ± 0.05	10.18 ± 0.06

Similarly, the oil yield is expressed as [48]:

$$-\ln \left(\frac{Y_i - Y_t}{Y_i} \right) = kt \quad (5)$$

where Y_i = percentage oil yield at 130 min and Y_t = percent oil yield at time t .

A plot of $\ln \left(\frac{Y_i - Y_t}{Y_i} \right)$ versus t is a straight line with k as the slope (Figure 4).

The mass transfer coefficient increases with increasing temperature due to decreasing resistance to mass transfer (Table 4). Increasing the temperature increases the Gibbs free energy, which elevates the chemical potential of the oil in the solid-liquid interphase.

The oil yield increases with temperature but remains constant after 333 K (Figure 5). The independence of the quantity of oil extracted from the temperature is distinct at 110 and 130 min. The constant value implies that the maximum amount of oil that can be extracted at a given time and temperature has been attained. Beyond 333 K, the results are similar to the trend reported in kinetics and thermodynamics studies on oil extraction from *Datura metel* L. [49].

Determination of activation thermodynamic parameters

The activation energy (E_a) and Arrhenius constant (A) are calculated from Equation (6) [35,50]:

Table 4. Mass transfer coefficient at varying temperatures.

Temperature, T (K)	k (min^{-1})
323	0.0119
328	0.0145
333	0.0164
338	0.0210

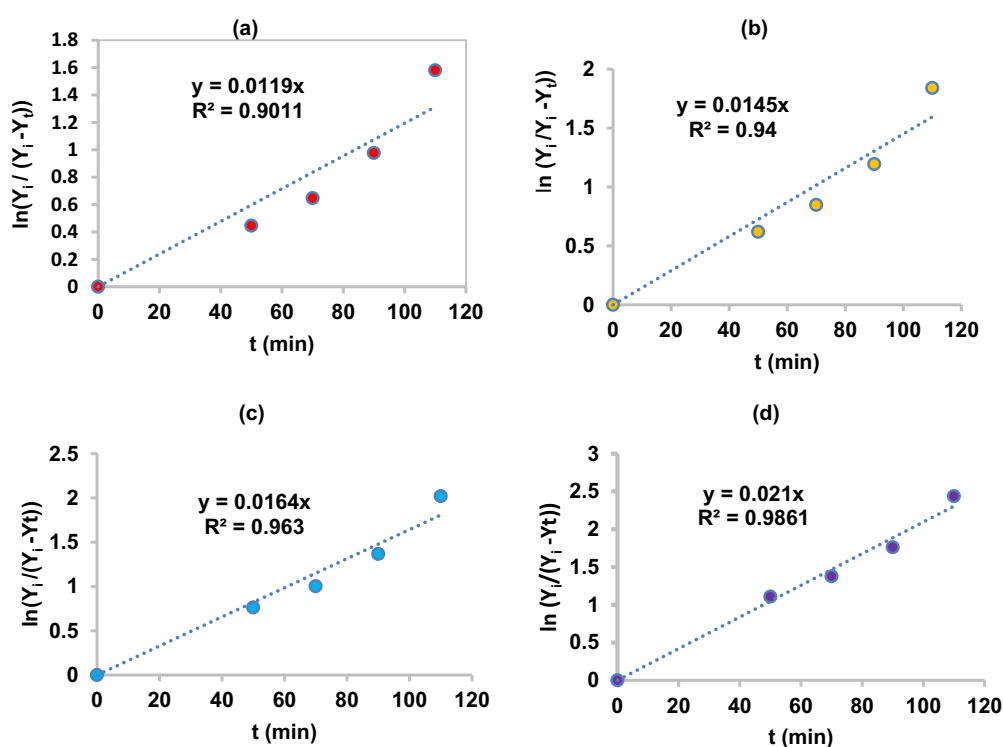


Figure 4. A plot of yield against time at (a) 323 K, (b) 328 K, (c) 333 K and (d) 338 K.

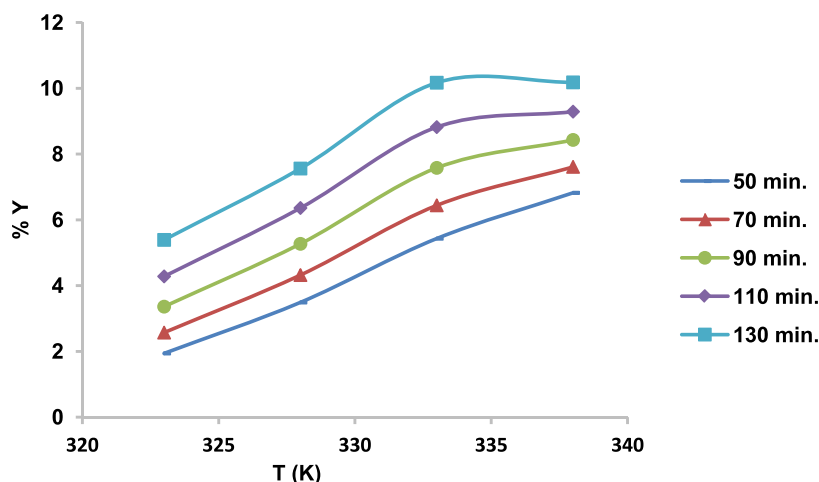


Figure 5. Plot of percentage yield versus temperature.

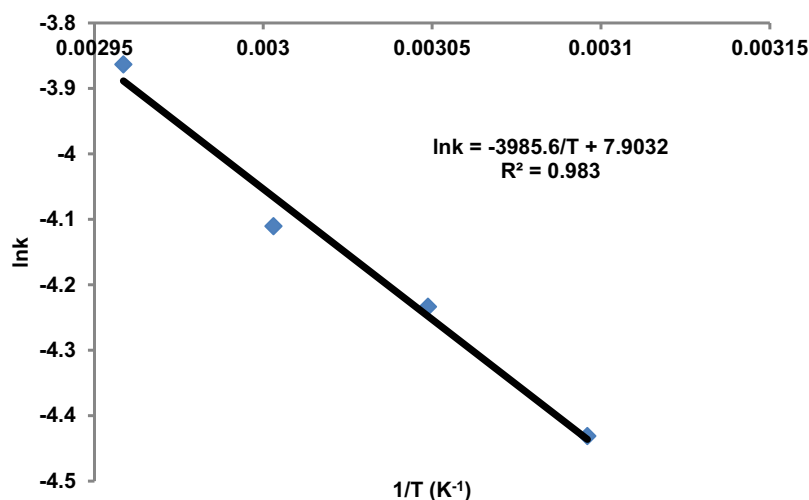


Figure 6. A plot of $\ln(k)$ versus $1/T$.

$$k = Ae^{-E_a/RT} \quad (6)$$

where R is the molar gas constant.

A plot of $\ln k$ versus $1/T$ is a linear graph whose slope and intercept are $-E_a/R$ and $\ln(A)$, respectively (Figure 6). The E_a is 33.14 kJ/mol. The activation energy is the minimum energy the oil must possess to be transferred within the solid-liquid interphase. Below this energy, it is very difficult for extraction to proceed. By comparison, the 33.14 kJ/mol is 15% lower than the value for *Chlorella* sp. [8]. This implies that oil extraction from the *Moringa* seed could be easier than from *Chlorella* sp. algae which has been highly explored.

The activation enthalpy (ΔH^\ddagger), activation entropy (ΔS^\ddagger) and activation Gibbs free energy (ΔG^\ddagger) are expressed as follows [34,35,50]:

$$A = \frac{RT}{N_A h} e^{\Delta S^\ddagger/R} \quad (7)$$

$$\Delta H^\ddagger = E_a - RT \quad (8)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (9)$$

where N_A = Avogadro's constant and h = Planck's constant.

The average ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger from 323 to 338 K are $-214.11 \pm 0.16 \text{ J (mol K)}^{-1}$, $30.39 \pm 0.05 \text{ kJ/mol}$, and $101.15 \pm 1.38 \text{ kJ/mol}$ (Table 5). The highly negative ΔS^\ddagger

Table 5. Activation parameters for the *Moringa* oil extraction.

$T(K)$	$\Delta S^\ddagger \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$	$\Delta H^\ddagger \text{ (kJ/mol)}$	$\Delta G^\ddagger \text{ (kJ/mol)}$
323	-213.92	30.45	99.55
328	-214.05	30.41	100.62
333	-214.18	30.37	101.69
338	-214.30	30.33	102.76

denotes a stiffer transition and dwindling internal energy content of the transition state, thereby slowing down the extraction. In addition, the impact of ΔH^\ddagger ($30.39 \pm 0.05 \text{ kJ/mol}$) as in Eyring's equation is analogous to E_a (33.14 kJ/mol) in the Arrhenius equation. Greater ΔH^\ddagger requires more energy which retards the extraction rate [51]. Obviously, the lower mass transfer coefficient ($0.0119\text{--}0.021 \text{ min}^{-1}$) and lower yield (10.18%) even at higher temperature and longer extraction time (333 K and 130 min) affirm a slower extraction rate. The respective ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger values are within -239.96 to $-309.3 \text{ J (mol K)}^{-1}$, $23.91\text{--}36.12 \text{ kJ/mol}$ and $6.3\text{--}105.39 \text{ kJ/mol}$ of the values observed in *Datura metel*, sunflower and *Jatropha curcas*, respectively [34,35,49].

Determination of thermodynamic parameters

The equilibrium constant (K), enthalpy change (ΔH), entropy change (ΔS) and change in Gibbs free energy (ΔG) are conveyed in Equations (10) and (11) [34,35]:

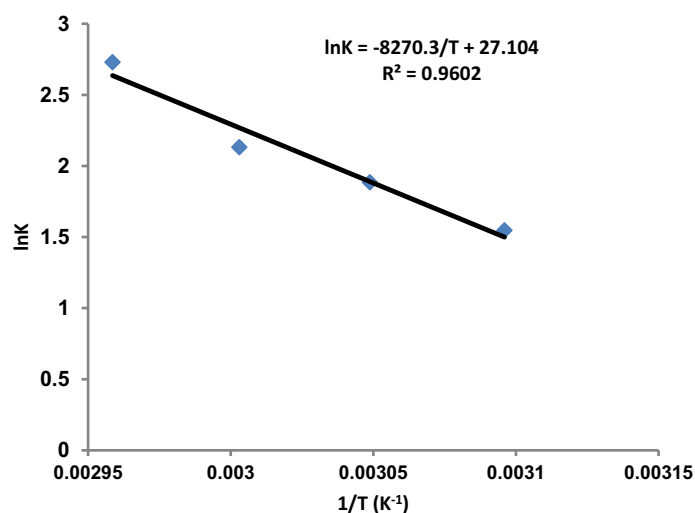


Figure 7. A plot of $\ln K$ versus $1/T$.

Table 6. Equilibrium constant and Gibbs free energy of the oil extraction at varying temperatures.

T(K)	K	ΔG (kJ/mol)
323	4.697	-4.065
328	6.586	-5.029
333	8.432	-5.775
338	15.333	-7.506

$$\frac{Y}{Y_u} = K = e^{kt} \quad (10)$$

$$\ln K = \frac{-\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (11)$$

where Y_u = percentage of unextracted oil.

Plotting $\ln K$ and $1/T$ at 130 min produced a straight line with slope $-\Delta H/R$ and intercept $\Delta S/R$ (Figure 7). The ΔH is 68.763 kJ/mol and ΔS is 22.1 J/(mol K)⁻¹. The enthalpy reveals the physico-chemical characteristics related to the internal energy of the oil-extraction system.

The ΔS portrays the degree of randomness during the extraction. The reaction is endothermic and irreversible, since ΔH and ΔS are positive.

Temperature plays an important role in oil extraction. Increasing the temperature by 5 K increases the equilibrium constant in the range of 1.8–6.9 (Table 6). As temperature increases, more oil is transferred from the solid phase to the liquid phase due to the increasing chemical potential of the oil in the solid and the more negative ΔG as in -7.506 kJ/mol.

The positive K and negative ΔG for all temperatures imply the extraction is a forward and spontaneous process, respectively. The results are within the range observed in sunflower seeds and *Jatropha curcas* [34,35].

Conclusions

We examine the kinetics and thermodynamics of *Moringa* oil extraction to produce biodiesel. The extraction yield is maximum (10.18%) at 338 K and 130 min. Transesterification enhances the crude oil's acid value, carbon residue and kinematic viscosity by 99.5%, 99% and 84%, respectively. The CN (67.12) and flash point (206°C) are 42.8% and 58.4%

higher, respectively, than the ASTM D6751 minimum value. The biodiesel pour point (-9°C) and CN imply that it can flow consistently even at -9°C, and will ignite suitably in compression engine. Considering the kinetics, the mass transfer coefficient seems lower (0.0119–0.0210 min⁻¹). From 110 to 130 min, the quantity of oil extracted is constant beyond 333 K. The thermodynamic parameters K , ΔH , and ΔS are positive whilst ΔG is negative, which respectively make the extraction a forward, endothermic, irreversible and spontaneous process. However, more energy is required for the extraction due to the greater value of ΔH^\ddagger (30.39 ± 0.05 kJ/mol). The highly negative ΔS^\ddagger (-214.11 ± 0.16 J/mol K) retards the extraction rate and yield because of the stiffer transition and dwindling internal energy content of the transition state. This is consistent with the slower mass transfer coefficient. Therefore, we find that *Moringa oleifera* oil is a good base oil to produce biodiesel, but the extraction process within 323–338 K results in low yield due to the stiff transition state and higher energy demand.

The study suggests that using smaller particle sizes of the powdered seed which would increase the surface area and mass transfer should be explored to improve the yield. A wider temperature range could also be studied using solvents other than hexane that have a higher boiling point.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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