



Kinetics and Thermodynamic Studies of Polyurethane Formation based on *Ximenia americana L* (Wild Olive) Seed Oil Monoglyceride and Different Diisocyanate

*SAMUEL, AE; SAMAILA, DS; IDRIS, U; HYELADZIRA, YB

Department of Chemistry, Federal University of Agriculture, Zuru, Kebbi State-Nigeria

*Corresponding Author: seaadeiza@yahoo.com

*ORCID: <http://orcid.org/0009-0001-5087-0069>

*Tel: +234-8032421643

Co-Authors Email: bondesamaila@gmail.com; idrisumar2010@gmail.com; ybwala1234@gmail.com

ABSTRACT: The renaissance of interest for renewable raw materials to replace petro-derived polyester or polyether-polyols used with diisocyanates in step-growth polymerization reactions for polyurethane production continues to dominate new frontiers. Accordingly, the objective of this paper was to prepare *Ximenia americana* seed oil monoglyceride, characterized the alcoholysis product for glycerides content, hydroxyl number and evaluate the kinetics and thermodynamics parameters for its copolymerization reactions with different diisocyanates in N, N'-dimethylformamide at varied isocyanate indices and temperatures using standard appropriate methods. The Results showed second-order rate constant (k), for the copolymerization reactions, with order TDI>HDI>MDI for diisocyanate reactivity with *X. americana* monoglyceride giving values up to $5.28 \times 10^{-3} \text{ Lmol}^{-1}\text{min}^{-1}$ for the TDI-based reaction at 1.50 isocyanate index and a corresponding average degree of polymerization (\bar{X}_n) of 28.49 at 80°C. The activation energy (E_a), activation enthalpy (ΔH_a) and entropy (ΔS^\ddagger), for copolymerization reaction are consistent with the order of reactivity of the diisocyanates, lowest values of E_a and ΔH_a with a corresponding highest values of ΔS^\ddagger for TDI-based copolymerization reaction at 1.02 and 1.50 isocyanate indices. The study has provided informative data on kinetic and thermodynamics parameters useful for the synthesis of polyurethane materials from *X. americana* seed oil-derived monoester and petro-based diisocyanates.

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The reaction of petro-based diisocyanates with polyether, polyester polyols or hydroxyl-terminated copolymer diol results in a polyurethane thermosetting or thermoplastic material Akindoyo *et al.*, (2016). Major products in the polyurethane industry, are elastomers, rubber, artificial leather, structural material, foam, coating for leather, wood, and metals Jozsef *et al.*, (2013); Samuel *et al.*, (2023). Kinetics of condensation reaction of polyol and diisocyanates has been studied using, indirect and direct methods. The former method measures a physical property that can be functionally related to the extent of reaction e.g.

Rheometry and Thermal techniques. In contrast, the latter measures the concentration of reactant or product species via Titrimetric and Spectroscopic analyses Zaverkina *et al.*, (2006); Cai *et al.*, (2008).

Spectroscopic techniques are more desirable methods in monitoring the kinetics of polyurethane preparation from copolymerization of hydroxyl-terminated molecules and diisocyanates via changes in isocyanate or urethane bands, indicating the extent of reaction. Using aromatic diisocyanates and hydroxyl-terminated polyether molecules, kinetics of

*Corresponding Author: seaadeiza@yahoo.com

*ORCID: <http://orcid.org/0009-0001-5087-0069>

*Tel: +234-8032421643

polyurethane reaction has been extensively investigated Schapman *et al.*, (2002); Jozsef *et al.*, (2013), and the kinetics, in the presence or absence of catalyst depicts a second-order model Sekker *et al.*, (2001); Ozkaynak, (2004); Uchimaru *et al.*, (2020). Temperature, catalyst-type and concentration, index of monomers, solvent and type of diisocyanate have been established as kinetic determinants for the reaction of a hydroxyl-terminated molecules and diisocyanates Draye *et al.*, (1999); Bumer *et al.*, (2001); Majid *et al.*, (2003). Kinetics of diisocyanate-diol reactions has been traditionally monitored by withdrawing and analyzing aliquots taken from the reaction mixture at regular time intervals, wherefrom, instantaneous isocyanate concentration was determined by quenching the aliquot with an excess amine solution, to cap terminal isocyanate and produce urea group *in situ*, and the unreacted amine protonated to an amine salt by back-titration with a mineral acid to determine the isocyanate concentration in the aliquot Ozkaynak, (2004); Bakare *et al.*, (2008). Reaction of an isocyanate with a hydroxyl-terminated molecule is described as a second-order model below 70% isocyanate conversion, beyond which a positive or negative deviation predominate Jozsef *et al.*, (2013). Positive deviations which is attributed to catalytic effect of hydroxyl groups, autocatalysis of the formed urethane groups and the formation of allophanate groups Ozkaynak, (2004); Jozsef *et al.*, (2013) are favored at high temperatures. On the contrary, negative deviations could be ascribed to increase in viscosity during copolymerization with corresponding Trommdorf-Norish effect Prenveille *et al.*, (2019), and relative reactivities of functional groups of participating monomers. *X. americana* plant belongs to the family Olacaceae, native to tropical Africa, its fruits are edible with seed kernel rich in polyunsaturated fatty acids Eromosele and Eromosele, (2002). The plant is known traditionally as; Tsada, Chabbuli, Anomadze and Igo in Hausa, Fulani, Tiv and Yoruba respectively Keay, (1989); Oladapo *et al.*, (2013). Polyether and polyester- polyols mostly in use for step-growth copolymerization reaction with diisocyanates to produce polyurethane materials are derivative of petrochemicals which are non-renewable and contribute immensely to global warming. In contrast, monoglyceride from vegetable oils are renewable resource, contribute less to carbon footprint and by extension confers on the polymer a variety of properties characteristic of the oil. The ever-increasing quest for environmental sustainability continues to elicit research interest for the need to seek raw materials for commodity polymers from bio-sources ostensibly to achieve biodegradability of polymers. Therefore, the objective of this paper is to prepare *Ximenia americana* seed oil monoglyceride,

characterized the alcoholysis product for glycerides content, hydroxyl number and evaluate the kinetics and thermodynamics parameters for its copolymerization reactions with different diisocyanates in N, N'-dimethylformamide at varied isocyanate indices and temperatures.

MATERIALS AND METHODS

Collection and pretreatment of Ximenia americana seeds: *X. americana* seeds were purchased from Kanya market, Danko-Wasagu Local Government Area of Kebbi State, cracked to obtain the seed kernel, washed under running water, dried under shade, milled to paste and packed in plastic container and stored in a refrigerator.

Extraction of X. americana seed oil: *X. americana* oil was extracted from the paste using a soxhlet extractor Eromosele and Eromosele, (2002) with slight modification. 200 g of ground *X. americana* seeds were packed in a soxhlet thimble and 1000 ml solvent (n-hexane) was poured into the 2 L soxhlet round bottom distillation flask. A condenser was connected to the top of the extractor. The heating mantle was set at 70 °C and heat was supplied to the distillation flask, to vaporize the solvent which later condensed in the packed thimble as admix with *X. americana* oil. After an exhaustive extraction process, *X. americana* oil was separated from n-hexane in a rotary evaporator (RE-100D).

Preparation of X. americana monoglyceride: The method as described by Samuel *et al.*, (2023) with slight modification was used to prepare the monoester. Briefly, *X. americana* seed oil was degummed by washing repeatedly with boiling water until the oil was non-sticky, the degummed oil was dried over silica gel for 72 h. The alcoholysis of *X. americana* seed oil was carried-out by aggregating the oil and glycerol (a trihydric alcohol) in a molar ratio of 1:3 in a fitted 1000 ml three- neck reaction round bottom flask with a thermometer, a stirrer and dry nitrogen gas inlet tube. 5 ml 0.1M NaOH (to saponify free fatty acid) was added, homogenized (450 rpm for 10 minutes) and heated on a thermostatic heating mantle to a temperature of 200°C for 30 minutes with continuous stirring (500 rpm), Ca(OH)₂ (0.15 wt % of the *X. americana* oil) was added as catalyst and the temperature raised to 250°C and maintained at this temperature for 6 h, after which an aliquot was withdrawn from the reaction mixture and tested for its solubility in methanol (solubility of reaction aliquot readily in methanol denote substantial conversion of triglyceride to monoglyceride). After cooling the reaction mixture to ambient temperature, it was dissolved with diethyl ether in a separatory funnel and

washed first with 0.2 M HCl solution and then repeatedly with distilled water to remove the catalyst and the residual glycerol. The ethereal layer was then dried over silica gel for 72 h. The residual diethyl ether was removed with the aid of a rotary evaporator (RE-100D).

Determination of hydroxyl value of *X. americana* monoglyceride: The hydroxyl value of *X. Americana* monoglyceride was determined using ASTM D 4274-88. 2 g of the *X. Americana* monoglyceride was weighed into a 250 ml glass-stopped Erlenmeyer flask. 5 ml of acetic anhydride was added to the flask, the flask was thoroughly but gently swirled for 5 minutes. 5 ml of acetic anhydride was measured into an empty flask (for the blank). The flasks were placed on a steam bath, under reflux condensers and heated for 1 h. 10 ml of distilled water was added to each flask, to hydrolyze excess acetic anhydride. The flasks were then cooled to ambient temperature and three drops of phenolphthalein added to each flask and titrated with 0.5 N ethanolic potassium hydroxide solution to a faint pink endpoint. The hydroxyl value and equivalent weight of polyol was calculated as in equation 1.

$$\text{Hydroxyl value} = \frac{[(B-S) \times N \times 56.1]}{W} \quad (1)$$

Where: B = is the volume of KOH solution required for blank; S = is the volume of KOH solution required for titration of the acetylated sample; W = is the weight of sample used for acetylation; N = is the normality of the ethanolic KOH solution.

Determination of α -monoglyceride content of *X. americana* monoglyceride: The α -monoglyceride content present in of *X. americana* monoglyceride was measured according to AOAC, 1992. 2.0 g of monoglyceride was weighed into a 100 ml glass-stopped volumetric flask. 50 ml and 25 ml of CHCl_3 and distilled water respectively, were aggregated to the flask and vigorously shaken for 60 seconds and allowed to stand for 1 h, the aqueous layer was siphoned into a 100 ml Erlenmeyer flask, 3 ml of glacial CH_3COOH was added to the residual sample in the flask and the aqueous layer extracted repeatedly until completely free of glycerol. The sample was then dried over silica gel for 48 h. 50 ml CHCl_3 and 50 ml acetic periodic acid was added to the previously dried sample contained in 250 ml volumetric flask. Two blanks were prepared, by adding 50 ml CHCl_3 and 50 ml distilled water (use as a check on the CHCl_3) to two 250 ml Erlenmeyer flasks, containing 50 ml acetic periodic acid respectively. The three volumetric flasks were homogenized (150 rpm for 30 min.) in a mechanical orbital flask shaker (Innova 2000). 20 ml

KI was aggregated to each flask and allowed to stand for 5 min. and the flasks were titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ until the brown iodine coloured aqueous layer disappeared. 2.0 ml of starch indicator was added to the solution and the titration continued until the disappearance of iodine from the CHCl_3 layer (indicative of the disappearance of the blue iodo-starch colour from the aqueous layer). Determination was done in triplicate. The α -monoglyceride content in terms of *X. americana* monoglyceride monoester was evaluated as in equation 2.

$$\% \alpha - \text{monoglyceride} = \frac{[(B-S) \times N \times 20.00]}{W} \quad (2)$$

Where: B = is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ used in blank titration; S = is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ used in sample titration; N = is the normality of $\text{Na}_2\text{S}_2\text{O}_3$ and W = is the weight of sample.

Column separation of *X. americana* alcoholysis product: To obtain a uniform phase solution before injection, *X. americana* monoglyceride sample was heated to 30°C in a thermostatic oil-bath for 10 minutes. The High Performance Liquid Chromatography with a pump (model 2350, ISCO, Lincoln, NE) and a photo diode array detector (Refracto Monitor IV; Thermo Separation Products, Riviera Beach, FL) was used to analyze the products. A Spherisorb ODS 2 column (250 4.6 mm, 80 mm pore size, 5 mm particle size; Waters, Milford, MA) was used for the separation. The temperature of the column was maintained at 35°C by a Brinkman RC 6 temperature bath (Westbury, NY). The mobile phase for the system was a 50:50 v/v mixture of acetone and acetonitrile and was degassed before use in the system. The mobile phase flow rate was set to 0.5 mLmin⁻¹. Data acquisition and analyses were performed using Hewlett-Packard (Wilmington, DE) Chemstation software. Monoglyceride, Diglyceride and Triglyceride standard were used to establish the calibration curves, which were used to quantify the content of these esters in the sample. All analyses were done in triplicates.

Determination of Kinetics of copolymerization of *X. americana* monoglyceride and different diisocyanates: Kinetics of polymerization of *Ximenia americana* monoglyceride and different diisocyanates was studied by a standard n-dibutylamine back-titration method Majid *et al.*, (2003); Bakare *et al.*, (2008). Monoglyceride corresponding to the required isocyanate index was weighed directly into a 250 ml three-neck round bottom reaction flask placed on a thermostatic mantle (Stuart, Germany), 20 ml N, N'-dimethylformamide and 0.001 wt%

Dibutyltindilaurate Sobhan *et al.*, (2002) compared to the weight of monoglyceride were added to the flask. The reaction flask was fitted with a stirrer, a nitrogen inlet tube, thermometer and reflux condenser. Calculated amount of diisocyanate (HDI and TDI) corresponding to the isocyanate index, was injected into the flask from a calibrated syringe or was weighed into the flask in the case of MDI flakes Samuel *et al.*, (2023), the thermostatic heating mantle set at the desired temperature, the stirrer was set at (100 rpm) and stop-clock switched on immediately. Aliquot was withdrawn at 30 minutes intervals using a graduated syringed pipette for kinetics study. The sample drawn out from the reaction mixture was injected into a pre-weighed 250 ml stopped conical flask containing 20 ml n-dibutylamine (to quench the copolymerization reaction). The flask was stopped, reweighed, swirled gently for 5 minutes and left to stand for 10 minutes. 50 ml methyl ethyl ketone / isopropyl alcohol mixture (1:1 v/v) was added, along with two drops of 0.1 % Bromocresol green indicator. Isopropyl alcohol allows methyl ethyl ketone and water to be miscible Rosu *et al.*, (2009). The blue content was titrated with 0.1 N HCl to a yellow end-point. Three blank titrations were carried out for each run taking 20 ml n-dibutylamine and 50 ml methyl ethyl ketone / isopropyl alcohol (1:1 v/v) mixture.

Concentration of residual -NCO was evaluated using the relation Majid *et al.*, (2003).

$$a - x = \frac{[(B-A) \times 0.042 \times NHCl]}{w} \quad (3)$$

Where B = volume of average blank titration in ml; A = volume of HCl required for titration of reaction mixture; a = initial concentration of isocyanate; x = instantaneous concentration of urethane product in terms of -NCO consumed; w = weight of aliquots drawn from the reaction mixture; (a-x) was evaluated from titration results and x computed there from. The extent of reaction and number of monomer unit on the polymer chain (degree of polymerization) were calculated using equations 4 and 5 respectively, Yunus *et al.*, (2004); Oladipo *et al.*, (2013).

$$P_{av} = \frac{x}{a} \quad (4)$$

$$\bar{X}_n = (1 - P_{av})^{-1} \quad (5)$$

Where, P_{av} = extent of reaction; \bar{X}_n = degree of polymerization.

The integral form, for a second-order reaction rate (equation 6) was used to plot the rate curves;

$$\left[\frac{1}{(a-b)} \right] \ln \left[\frac{b(a-x)}{a(b-x)} \right] = Kt \quad (6)$$

Where, a = initial concentration of isocyanate; b = initial concentration of polyol; x = instantaneous concentration of urethane product in terms of -NCO reacted; k = rate constant; t = time of reaction.

The slope of $\left[\frac{1}{(a-b)} \right] \ln \left[\frac{b(a-x)}{a(b-x)} \right]$ vs t produces the second-order rate constant.

Determination of thermodynamic parameters of copolymerization of X. americana monoglyceride and different diisocyanates: The energy of activation (E_a), enthalpy of activation (ΔH_a) and entropy (ΔS^*) are the thermodynamic parameters of the copolymerization reaction, determined using the Arrhenius and Eyring equations. The energy of activation was determined using the simplified form of Arrhenius equation as shown in Tables 7 and 8

$$K = Ae^{-\frac{E_a}{RT}} \quad (7)$$

$$\ln K = \ln A - \frac{E_a}{RT} \quad (8)$$

Where k, A and E_a are the second-order rate constant, frequency factor and energy of activation respectively. R = molar gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the reaction temperature expressed in Kelvin.

The values of E_a for the copolymerization reaction were calculated from the slopes ($-\frac{E_a}{R}$) of Arrhenius plots ($\ln k$ vs $1/T$). Eyring-Polanyi relationship (equation 9) Espenson, (1990) was used to determine the activation enthalpy (ΔH_a) and entropy (ΔS^*) of the copolymerization reaction.

$$\ln \frac{k}{T} = \ln \frac{R}{Nh} + \frac{\Delta S^*}{R} - \frac{\Delta H_a}{RT} \quad (9)$$

Where, T is the reaction temperature in Kelvin, R = the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), k = is the second-order rate constant, N = is the Avogadro's constant (6.02×10^{23}) and h = is the Planck's constant ($6.62 \times 10^{-34} \text{ Js}$).

The values of ΔH_a and ΔS^* were deduced from the slope ($-\Delta H_a/R$) and intercept ($\ln R/Nh + \Delta S^*/R$) respectively from the plots $\ln k/T$ vs $1/T$.

RESULTS AND DISCUSSION

The glycerides content and hydroxyl number from alcoholysis of *X. americana* seed oil are presented in table 1. The monoglyceride content (53.52%) for *X. americana* monoglyceride exceeds 48.30% reported

for rubber seed oil monoglyceride Bakare *et al.*, (2008), but lower than 90.1% as reported for palm oil monoglyceride Tanaka *et al.*, (2008). The higher monoester content for *X. americana* over that for rubber seed oil may be attributed to the following; removal of phospholipid compounds notable for their counter emulsifying properties, during the degumming process Yunus *et al.*, (2004); Stirna *et al.*, (2012), the availability of more glycerol molecule for transesterification, owing to low free fatty acid (8.05 %) content of *X. americana* seed oil Eromosele and Eromosele, (2002) compared to (21.40 %) for rubber seed oil Bakare *et al.*, (2008) and the soap molecules formed insitu during the neutralization of *X. americana* seed oil free fatty acid by caustic soda, act

as emulsifier Cai *et al.*, (2008), by lowering surface tension and improves the interplay of trihydric alcohol and *X. americana* triglycerides molecules, coherent with increased quantity and better quality of *X. americana* monoglyceride produced. Consequently, the hydroxyl number and α - monoglyceride content of 194.30mgKOH/g and 36.51% respectively, for *X. americana* monoglyceride are higher compared to 183.15 mgKOH g⁻¹ and 29.41% for rubber seed oil monoester Bakare *et al.*, (2008). Moreover, the hydroxyl number for *X. americana* monoglyceride is within range (160-1000 mgKOH g⁻¹) technically required for polyols used for production of elastomers and flexible foam in the polyurethane industry Zhang *et al.*, (2007); Campanella *et al.*, (2009).

Table1: Glycerides Composition and Hydroxyl number of *X. americana* Alcoholysis Product

Component	Monoglyceride (%)	Diglyceride (%)	Triglyceride (%)	α -Monoglyceride (%)	OH Number (mgKOH/g)
Content	53.52±1.21	34.89±0.72	11.59±1.05	36.51±1.33	194.30±2.08

Table 2: Effect of temperature on copolymerization of *X. americana* monoglyceride and diisocyanates at 1.02 isocyanate index.

Reaction	Temperature(°C)	$k \times 10^3$ (Lmol ⁻¹ min ⁻¹)
TDI-based-1.02	40	0.18
HDI-based-1.02	40	0.09
MDI-based-1.02	40	0.06
TDI-based-1.02	50	0.21
HDI-based-1.02	50	0.11
MDI-based-1.02	50	0.07
TDI-based-1.02	60	0.29
HDI-based-1.02	60	0.15
MDI-based-1.02	60	0.11
TDI-based-1.02	70	0.46
HDI-based-1.02	70	0.25
MDI-based-1.02	70	0.17
TDI-based-1.02	80	0.72
HDI-based-1.02	80	0.34
MDI-based-1.02	80	0.23

Table 3: Effect of temperature on copolymerization of *X. americana* monoglyceride and diisocyanates at 1.50 isocyanate index.

Polyurethane sample	Temperature(°C)	$k \times 10^3$ (Lmol ⁻¹ min ⁻¹)
TDI-based-1.50	40	1.05
HDI-based-1.50	40	0.54
MDI-based-1.50	40	0.36
TDI-based-1.50	50	1.23
HDI-based-1.50	50	0.62
MDI-based-1.50	50	0.40
TDI-based-1.50	60	2.08
HDI-based-1.50	60	1.06
MDI-based-1.50	60	0.79
TDI-based-1.50	70	4.36
HDI-based-1.50	70	2.18
MDI-based-1.50	70	1.45
TDI-based-1.50	80	5.28
HDI-based-1.50	80	2.66
MDI-based-1.50	80	1.77

The second-order rate constants (k) for the copolymerization reaction at varied diisocyanate index and temperature were calculated from the initial linear portions of the kinetic plots shows significant variation in reaction rates as represented in tables 2 and 3. It's evident that the second-order rate constants for the

polymerization reaction of diisocyanates with *X. americana* monoglyceride are in the order TDI>HDI>MDI at all temperatures and diisocyanate indices giving values up to 5.28×10⁻³ Lmol⁻¹min⁻¹ for TDI at 80°C and at 1.50 isocyanate index. This suggest a more pronounced positive deviation and

autocatalytic effect of the preponderance urethane group in the aromatic diisocyanate based copolymerization reaction Bumer *et al.*, (2001); Majid *et al.*, (2003). Furthermore, for each diisocyanate, the rate constant increases with temperature by as much as 4-fold in the range 40-80°C at 1.50 isocyanate index. Similarly, the rate constant increases with isocyanate index (1.02-1.50) for all diisocyanate-type by a factor of eight for TDI-based reaction at 70°C.

In general aromatic diisocyanate are more reactive than aliphatic and cyclo-aliphatic diisocyanates as a result of the inductive delocalization of electron pair or negative charge on the nitrogen into benzene ring, making the carbon atom of the isocyanate moiety more prone to nucleophilic addition reaction Uchimarū *et al.*, (2020). This is consistent with the polymerization of poly (butadiene-acrylonitrile) copolymer diol separately with 4-4'-methylene diphenyl diisocyanate and hexamethylene diisocyanate, which gave second-order rate constant for polyurethane formation in two-orders magnitude higher for the former consonance with the greater reactivity of aromatic diisocyanates Eromosele, (1981).

Therefore, the above order of reactivity for diisocyanates having aliphatic (HDI) more reactive than MDI, does not fit into this expectation. However, the order of reactivity may be explained as arising from a combination of steric factors. That is the predisposition of MDI to oligomerization Zlatanić *et al.*, (2004), which occludes the isocyanate groups accentuating steric effects, in their reactions with diol, a monoglyceride with a pendant fatty acid acyl chain which interfere sterically with reactivity of the hydroxyl groups. The latter effect is expected to be more acute with respect to MDI a bulky diisocyanate. Thus, the steric effects, in reduced reactivity of MDI, is more pronounced than the expected reduction in reactivity of HDI, by electron-donating inductive effects of the methylene groups. Reaction rate constants for polyurethane formation in toluene based on polyol from castor oil using TDI, IPDI and HDI in the temperature range 40-60°C. the order of reactivity of the diisocyanate was TDI>HDI>IPDI consistent with the greater reactivity of aromatic diisocyanate compared to the aliphatic diisocyanates, yielding rate constants in the range $2.0-32 \times 10^{-4} \text{ Lmol}^{-1}\text{s}^{-1}$, the highest value being for TDI at 60°C Hablot *et al.*, (2008). No direct comparison can be made between the results for TDI and HDI using castor oil and *X. americana* monoester as sources of hydroxyl-terminated molecules because of differences in experimental conditions, notably, the solvent- toluene and $\text{N}_2\text{N}'$ -dimethylformamide respectively. However, it sufficient to note that the rate constants as reported

for castor- based copolymerization are much higher than those for *X. americana* monoglyceride. This could be ascribed to presence of *X. americana* diglyceride and triglyceride-molecules in the latter reaction medium, as these esters could pose steric hindrance and reduce reaction rates of hydroxyl and isocyanate moieties in *X. americana* monoglyceride and diisocyanate respectively. Thus, it's justifiable that separation of the diester and residual triester in the alcoholysis product of *X. americana* seed oil using appropriate analytical instrumentation could enhance a better reactivity of the preponderant primary hydroxyl groups in *X. americana* α -monoglyceride with diisocyanates compared to lower reactive secondary hydroxyl groups anchored on the fatty acid acyl chains in castor oil.

Table 4: Degree of polymerization and extent of reaction at 40°C and isocyanate index of 1.02

Time (min.)	HDI-based-1.02		TDI-based-1.02		MDI-based-1.02	
	P _{av} (%)	\bar{X}_n	P _{av} (%)	\bar{X}_n	P _{av} (%)	\bar{X}_n
30	15.04	1.17	17.40	1.21	11.73	1.13
60	24.95	1.33	26.88	1.37	17.75	1.22
90	38.13	1.62	41.12	1.71	26.47	1.36
120	42.00	1.72	45.18	1.82	37.58	1.60
150	54.15	2.18	56.08	2.28	45.05	1.82

Table 5: Degree of polymerization and extent of reaction at 80°C and isocyanate index of 1.02

Time (min.)	HDI-based-1.02		TDI-based-1.02		MDI-based-1.02	
	P _{av} (%)	\bar{X}_n	P _{av} (%)	\bar{X}_n	P _{av} (%)	\bar{X}_n
30	28.97	1.41	34.65	1.53	22.66	1.29
60	48.28	1.93	55.75	2.26	40.46	1.68
90	65.39	2.89	68.38	3.16	45.72	1.84
120	74.08	3.86	75.13	4.02	59.67	2.48
150	80.86	5.22	81.79	5.49	70.52	3.39

Table 6: Degree of polymerization and extent of reaction at 40°C and isocyanate index of 1.50

Time (min.)	HDI-based-1.50		TDI-based-1.50		MDI-based-1.50	
	P _{av} (%)	\bar{X}_n	P _{av} (%)	\bar{X}_n	P _{av} (%)	\bar{X}_n
30	19.72	1.25	22.97	1.31	14.20	1.17
60	33.36	1.50	36.93	1.59	27.20	1.37
90	48.26	1.93	53.44	2.15	35.10	1.54
120	71.56	3.52	74.18	3.87	55.52	2.25
150	88.13	8.42	90.29	10.31	61.05	2.57

Table 7: Degree of polymerization and extent of reaction at 80°C and isocyanate index of 1.50

Time (min.)	HDI-based-1.50		TDI-based-1.50		MDI-based-1.50	
	P _{av} (%)	\bar{X}_n	P _{av} (%)	\bar{X}_n	P _{av} (%)	\bar{X}_n
30	63.18	2.72	68.23	3.15	57.04	2.33
60	74.15	3.87	80.60	5.15	68.16	3.14
90	88.55	8.87	93.89	16.37	82.43	5.69
120	91.16	11.31	95.55	22.47	85.46	6.88
150	92.14	12.72	96.49	28.49	86.00	7.14

The extent of reaction (P_{av}) and degree of polymerization (\bar{X}_n) evaluated for the copolymerization of *X. americana* monoester and different diisocyanate at varied isocyanate index at temperatures 40 and 80°C are shown in Tables 4-7. The extent of reaction (P_{av}) increases with temperature for the diisocyanate-mono glyceride reaction yielding values of 96.49, 92.14 and 86.00 % for TDI, HDI and MDI-based reactions respectively at 1.50 isocyanate index and 80°C at 150 min. reaction time. This is internally consistent with the corresponding rate constants previously mentioned which showed greater reactivity of TDI-based reaction. The average degree of polymerization (\bar{X}_n), increases with isocyanate index i.e. for TDI-based copolymerization with *X. americana* monoester, having values of 5.49 and 28.49 for 1.02 and 1.50 isocyanate indices respectively at 80°C and 150 min. reaction time. However, the average degree of polymerization is generally low for all the copolymerization reaction, the highest value of 28.49 being less than the range 50-100 reported for preparation of useful uncrosslinked polymers Odion, (2004). Besides, the range 8.32-10.64 reported for polyurethane based on 1, 6- hexamethylene diisocyanate and poly (carbonate-co-ester) diol Fernandez-d'Arlas *et al.*, (2007), which is lower relative to HDI-based reaction with *X. americana* monoglyceride at 80°C and 1.50 isocyanate index, could be ascribed to steric factor accentuated by the bulkiness of the copolymer diol.

Table 8: Thermodynamic parameters for *X. americana* monoglyceride and different diisocyanates.

Reaction	E_a (KJ mol ⁻¹)	ΔH_a (KJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)
TDI-based-1.02	23.82	27.87	-200.40
HDI-based-1.02	43.75	29.78	-205.06
MDI-based-1.02	47.43	30.29	-211.99
TDI-based-1.50	42.80	32.06	-186.43
HDI-based-1.50	62.50	36.87	-198.71
MDI-based-1.50	86.24	39.00	-202.73

Thermodynamic data are presented in table 8 and the Eyring-Polanyi plots for derivation of enthalpy (ΔH_a) and entropy (ΔS^*) for the copolymerization of *X. americana* monoglyceride and different diisocyanates are shown in figures 1 to 6. The R^2 values 96 to 98% correlations as evident in the plots, indicates, the participating hydroxyl and isocyanate moieties demonstrate greater affinities irrespective of their molecular backbone orientation Fernandez-d'Arlas *et al.*, (2007); Uchimaruru *et al.*, (2020). The activation energies for reactions at different isocyanate index are

consistent with the order of their reactivities, lowest in each case for the TDI-based reaction. However, the higher values of activation energies for the copolymerization reaction at 1.50 isocyanate index are not consistent with the observed increased rate of reaction as the index is increased from 1.02 to 1.50. The inconsistency is reconciled by the understanding that at higher isocyanate index of 1.50, secondary reactions, especially; formation of urea, biuret and allophanate, outside of polyurethane formation may occur to increase the observed overall rate of reaction. Furthermore, the lower values of E_a and ΔH_a in concordance with higher values of ΔS^* for the HDI-based reactions relative to the MDI- based systems could be ascribed to the symmetrical character of the participating monomers in the former compared to asymmetrical monomers orientation in the latter. In addition, the flexible methylene groups in HDI with primary isocyanate moieties and the remarkable proportion of aliphatic α - monoglyceride content in *X. americana* monoester with primary hydroxyl groups, implies a more dispersed reactive moieties within the reaction medium that easily lend themselves to copolymerization. For copolymerization in toluene based on castor polyol at isocyanate index of 1.0, the activation energies using TDI and HDI were 80 and 60 KJmol⁻¹ respectively Hablot *et al.*, (2008). These are significantly higher than observed in the present study conducted for *X. americana* monoglyceride in N, N'-dimethylformamide at isocyanate index of 1.02. There is a correlation between the activation energies for the copolymerization reactions and corresponding entropy of activation (ΔS^*), high negative values of ΔS^* corresponding to low activation energies for values at different isocyanate index. Besides, the reduced values of ΔS^* and highest values of E_a and ΔH_a at both isocyanate indices for the MDI-based reactions, compared to those for TDI and HDI-based systems could be attributed to contributory steric factors from cyclization and polycyclotrimerization of MDI, occasioned by the relative reactivities of the isocyanate moieties Lucio *et al.*, (2016). The characteristic spatial distributions of these molecules in the reaction medium, implies the system is less disordered, but requires a greater internal energy for the reaction to proceed. Therefore, the chemical merit of this is in consonance with immense benefits of material properties, as the exothermic copolymerization reaction of MDI and *X. americana* monoglyceride could be kinetically and thermodynamically controlled more effectively than those for TDI and HDI-based reactions to produce polymer materials with larger internal volume space for molecular flexibility and heterocyclic ring oligomers in the microstructure of the polymer most consistent with physico-mechanical properties and

enhanced thermal resistance Micheal and Markus, (2018); Samuel *et al.*, (2023).

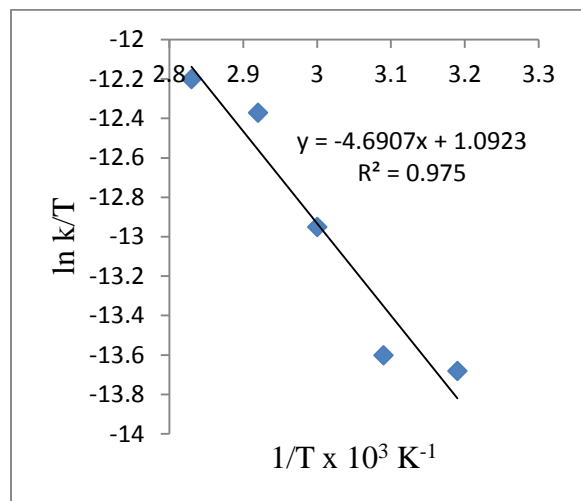


Fig 1: Eyring-Polanyi plot for MDI-based-1.50 reaction

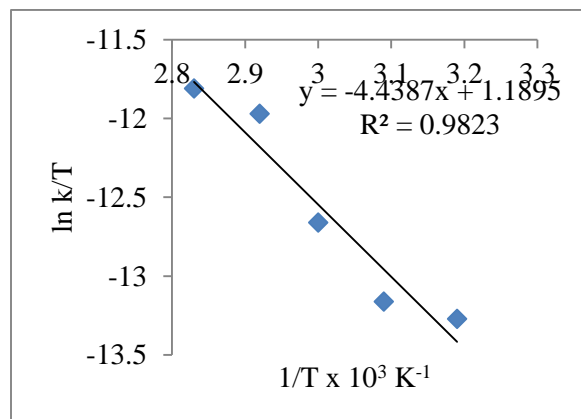


Fig 2: Eyring-Polanyi plot for HDI-based-1.50 reaction

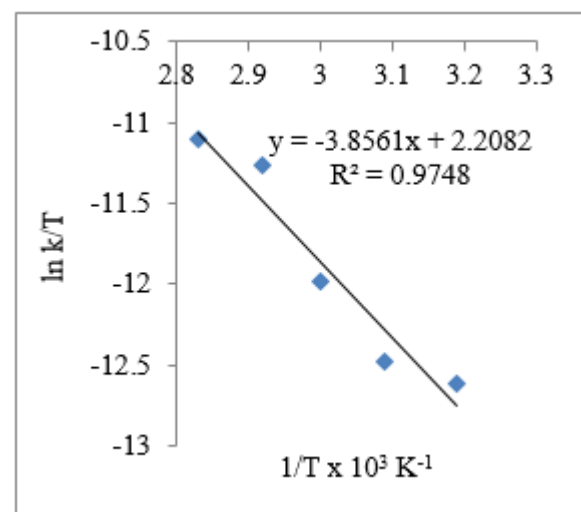


Fig 3: Eyring-Polanyi plot for TDI-based-1.50 reaction

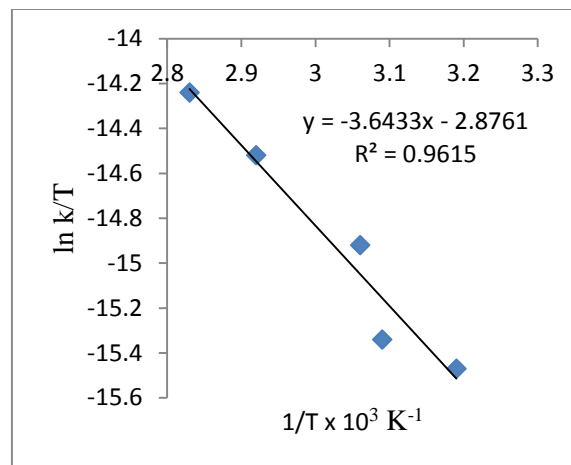


Fig 4: Eyring-Polanyi plot for MDI-based-1.02 reaction

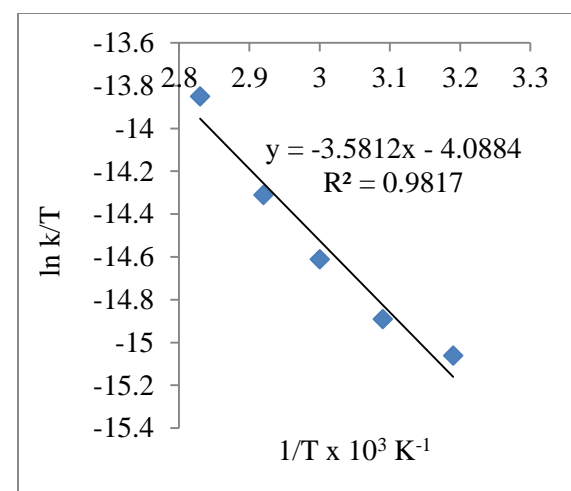


Fig 5: Eyring-Polanyi plot for HDI-based-1.02 reaction

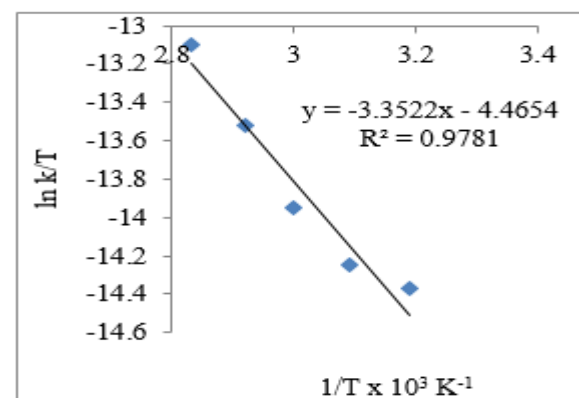


Fig 6: Eyring-Polanyi plot for TDI-based-1.02 reaction

However, practical application notably in preparation of coatings where ultraviolet stability is imperative, aromatic and cyclo-aliphatic diisocyanates does not sit well from a technical standpoint, as rearrangement reactions of urethane group around the aromatic ring occasioned by photo-fries from UV light produces a

coloured quinone-imide structure Rosu *et al.*, (2009). Hence, HDI-based copolymerization with *X. americana* monoglyceride will be more suitable for preparation of UV-stable polyurethane materials and waterborne polyurethane coatings.

Conclusion: The kinetic and some thermodynamic parameters of the copolymerization reactions of *X. americana* monoglyceride with different diisocyanate in N, N'-dimethylformamide at varied isocyanate indices and temperatures have been studied. The reactions were second-order characterized by TDI>HDI>MDI order of diisocyanate reactivity with *X. americana* monoester. The kinetic and thermodynamic parameters for the reactions, presents *X. americana* monoglyceride as a derived bioresource industrial feed stock with auspicious potentials for development of polyurethane materials with specialty application.

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Data Availability Statement: Data are available upon request from the corresponding author or first author.

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