Ethyl esters of fatty acids and thermophysical properties of biodiesel derived from *Ceiba pentandra*L. seed oil acclimatized in Benin and biodiesel-diesel blends

Papin Sourou MONTCHO[1,2,3], Guevara NONVIHO[1,4], Jean-Patrick BAZILE[2], Cokou Pascal AGBANGNAN DOSSA[1], Anna CHROSTOWSKA[3], David BESSIERES[2] and Dominique C. K. SOHOUNHLOUE[1*]

[1]*Research Unit on Molecular Interactions, Study and Research Laboratory in Applied Chemistry of the Polytechnic School of Abomey-Calavi, University of Abomey-Calavi (URIM / LERCA / EPAC / UAC), 01 BP: 2009 Cotonou , Benin.*
[2]*Laboratory of Complex Fluids and their Reservoirs, Multidisciplinary Institute for Applied Reseach in Petroleum Engineering, University of Pau and Pays de l'Adour (LFCR / IPRA / UMR 5150 / E2S UPPA), 64000, PAU, France.*
[3]*Institute of Analytical and Physicochemical Sciences for the Environment and Materials, University of Pau and Pays de l'Adour (IPREM / UMR 5254 / E2S UPPA), 64000, Pau, France.*
[4]*Multidisciplinary research laboratory on technical education, National University of Engineering, Mathematical and Technological Sciences, Lokossa BP 133, Benin.*

Abstract:
Background:*Fatty acid composition and knowledge of properties such as density and kinematic viscosity are paramount both for optimizing diesel engine operation and for specification of fuel quality. The objective present work is to study the thermophysical and chemical properties of biodiesel as well as blends (B5, B10, B20) of biodiesel with diesel for their transferability as alternative diesel. The Biodiesel has been formulated from the seed oil ceiba pentandra by the transesterification reaction.*
Materials and Methods*: Density of samples was evaluated at pressures up to 40MPa and varying the temperature from 293.15K to 353.15K. Kinematic viscosity of samples was measured at atmospheric pressure in a temperature range from 293.15K to 373.15K and presented in this work. Density values were fitted from the modified Tait-like equation with absolute mean deviations of approximately 0.005%.*
Results*: Biodiesel derived from seed oil from Ceiba pentandra and blends of 5%, 10% and 20% of biodiesel with diesel were examined. Main constituents of formulated biodiesel are palmitate (C16: 0) (24.53%), oleate (C18: 1) (19.6%) and linoleate (C18: 2) (36.92%) esters.Density and kinematic viscosity of biodiesel are greater than those of biodiesel-diesel blends and decrease with increasing temperature. Density and kinematic viscosity of blends decrease with proportion or amount of biodiesel in the blends in that order (B5 <B10 <B20). Isothermal compressibility of samples increases with temperature at constant pressure and decreases as pressure increases along isotherm. Absolute mean deviations between the measured densities and those calculated usingTait-Like equation for our samples examined at around 0.005% and confirm the accuracy of modeling and reliability of values of isothermal compressibility calculated.*
Keywords*:Ceiba pentandra; biodiesel; bleeds; thermophysical properties and isothermal compressibility.*

I.   Introduction

The progressive depletion of fossil resources has prompted the search for a new source of alternative energy[1]. Among these alternative sources, bioenergy in general and biofuels in particular are the most popular because of the drawbacks associated with the use of fossil fuels. One of the options for replacing fossil diesel is biodiesel, an excellent substitute for diesel fuel which is currently widely used in transportation. In fact, biodiesel is generally produced by a transesterification reaction, where the triglycerides contained in vegetable oils or animal fats react with an alcohol in the presence of a catalyst[2,3]. Alkyl esters of fatty acids are the products of the transesterification reaction[4].The methyl and ethyl esters obtained after the transesterification reaction are the closest to biodiesel. However, about 95% of biodiesels produced today are produced with vegetable oils that compete with human food[5].The result is an ongoing debate on the use of agricultural land for energy purposes as well as a growing concern for global food security[6,7]. For these reasons, the scientific

community is studying the possibility of using unconventional feedstocks for the production of biodiesel. The use of unconventional vegetable oils as fuel in diesel engines has been considered, but their relatively high density and kinematic viscosity and low volatility cause problems in the combustion chamber. Biodiesel is an interesting and credible alternative to reduce dependence on petroleum-derived fuels. Indeed, it is accepted that the use of pure biodiesel instead of diesel allows a reduction in carbon dioxide (CO_2) emissions of around 90%. Compared to fossil fuels, biodiesel is very low-polluting, easily biodegradable and presents little risk to the environment. Regardless of its origin, biodiesel contains only traces of sulfur. In addition to these other advantages, such as its high lubricity, engines that use it run longer. Today, biodiesel can be blended with pure diesel in any percentage. Biodiesel blends of 2% to 20% can be used in most diesel equipment with little or no modification[8]. A number of researchers have adopted this approach and have implemented these fuels in diesel engines. Srithar et *al* (2014) blended diesel with *Pongamia pinnata-mustard* biodiesel at different ratios[9]. They found an improvement in the physico-chemical properties, which translates into an increase in the calorific value, density and viscosity of the mixtures compared to those of diesel fuel. Benjumea et *al* (2008) measured the density and kinematic viscosity of biodiesel and palm oil blends at different temperatures (289-373 K) and at five biodiesel concentrations[10]. They found that density was a linear function of temperature for palm oil biodiesel, diesel and blends. In addition, they found that the kinematic viscosity varied exponentially with decreasing temperature in all cases. In general, blending biodiesel with diesel gives biodiesel-like physical-chemical properties. For the correct development of engine combustion models, it is necessary to know the chemical composition and thermophysical properties of biodiesels and their blends with pure diesel[11]. Furthermore, the understanding and knowledge of these properties as a function of temperature and pressure are particularly important for their application in the engine industry and in the search for new renewable energies.
The species *Ceiba pentandra* (L) known as Kapokier is a large tree belonging to the Bombacaceae family, which is widespread in tropical areas. Kapokier is known for its soft white silk[12,13]. It is a large tree 35-60 meters high with conical spines on the trunk and branches. It is fast growing and becomes productive in 4 to 5 years. Under optimal conditions an adult tree can produce up to 400 fruits in a year, giving 15-18 kilograms of fiber and about 30 kilograms of seeds per fruiting[14]. The fruit is in a fusiform membranous envelope of 10-30 x 3-15 centimeters containing black spherical seeds representing about 28% m/m of the fruit and covered with fine silky hairs. The seeds are a source of oil and therefore an excellent raw material in the paint and biodiesel production industries[15].

In this study, the unconventional seeds oil of *Ceiba pentandra* (L.) was converted to ethyl esters by the transesterification reaction in basic catalysis. The fatty acid profile of the oil was also determined. Density was measured using a vibrating tube technique for *Ceiba pentandra* ethyl biodiesel in a pressure range of 0.1 to 40 MPa and kinematic viscosity at temperatures ranging from 293.15 to 353.15 K. The isothermal compressibility of biodiesel and biodiesel-diesel blends up to 40 MPa and from 293.15 K to 353.15 K was determined from density measurements. Density and compressibility are essential properties because injection systems, pumps and injectors must deliver the precise amount of fuel to ensure proper combustion. The experimental density data were correlated using a Tait-Like equation, resulting in an excellent representation of the data set over the entire temperature and pressure range. The kinematic viscosity values of the different samples were corrected from the kinetic energy equation.

II. Material And Methods
The biodiesel studied in this work was produced by the transesterification reaction from non-edible seed oil of *Ceiba pentandra* acclimatized in Benin. Indeed, seed oil was extracted from *Ceiba pentandra* seeds collected in North-West of Benin 9° 39′ 42″ North then 1° 23′ 05″ East. Part of the formulated ethyl biodiesel was used to prepare pure biodiesel-diesel blends. Thus, the blends were prepared at 20°C in an Erlenmeyer flask with a lid under magnetic stirring at 250 rpm for 10 min. *Ceiba pentandra's* ethyl biodiesel was blended with the pure diesel in three proportions: 5%, 10% and 20% by volume. These blends were named B5, B10 and B20 respectively.

Physico-chemical properties and fuels
The refractive index of the samples was determined by an Anton Paar refractometer according to the method described in NB ISO 6320 (2006) with an accuracy of $\pm$ 2×10-5 nD at 293.15 K. The cetane number was calculated according to the equation proposed by Knothe[16].The cetane number of each fatty acid ethyl ester is obtained from[17].

$$CN_i = -7.8 + 0.302 \times M_i - 20 \times N \qquad (Error! \ Bookmark \ not \ defined.)$$

Where CN_i represents cetane number of ith fatty acid ethyl ester.

The kinematic viscosity (η_i) and density (ρ_i) of each fatty acid ethyl ester are obtained respectively following equations (2) and (3). The kinematic viscosity (η_i), density (ρ_i) and higher heating value (ω_i) of each fatty acid ethyl ester are obtained respectively following equations (2), (3) and (4)[17].

$$\ln(\eta_i) = -12.503 + 2.496 \ln(M_i) - 0.178 \times N \qquad (\text{Error! Bookmark not defined.})$$

where η_i is the kinematic viscosity at 40°C of the ith fatty acid ethyl ester in mm^2/s.

$$\rho_i = 0.8463 + \frac{4.9}{M_i} + 0.0118 \times N \qquad (\text{Error! Bookmark not defined.})$$

where ρ_i is the density at 20°C of the ith fatty acid ethyl ester in g/cm^3.

$$\Delta_i = 46.19 - \frac{1794}{M_i} - 0.21 \times N \quad (\text{Error! Bookmark not defined.})$$

where Δ_i is the higher heating value of the ith fatty acid ethyl ester in MJ/kg.

M_i represents the molecular weight of the ith fatty acid ethyl ester and N, the number of double bonds in a given fatty acid ethyl ester. N is zero, one, two and three for methyl ester C18:0, C18:1, C18:2 and C18:3 respectively.

Analyses were performed according to the standard test method described by ASTM D93 standards for flash point[18], ASTM D97 for pour point[19], ASTM D664 for the acid value[20], the iodine index expressed in mg I_2/100g was determined according to the EN14111 standard. The results were compared to the limit values of the American (ASTM)[21,22] and European (EN 14214)[23] standards for biodiesel.

Procedure methodology
Determination of fatty acid composition by GC/MS
The fatty acid profile was determined for the unconventional seed oil investigated. For this purpose, the sample of this oil was previously converted to fatty acid ethyl ester.
Preparations of ethyl esters of fatty acids (EEAG)
400µL of the solution of KOH (85%, Sigma Aldrich) 2 N in ethanol (99.8% (GLC) for CPL-HP, Fischer Scientific) is mixed with 60 mg of oil; the mixture is refluxed at 70°C and under vigorous agitation. After one hour of reaction, the reaction mixture was cooled to room temperature. Then 5 ml of n-heptane (Pesti-S grade, Biosolve) and 1 g sodium sulfate were added to this mixture, vortexed for 10 seconds and left to stand for 20 min. The ethyl esters dissolved in heptane formed the top layer which was separated from the glycerol decanted at the bottom of the target tube. 100 µL of ethyl esters extracted from the top layer was diluted in 900 µL with n-heptane for analysis.

Analysis conditions
The fatty acid profile of the unconventional vegetable seed was carried out by a GC Scion 486 coupled to timsTOF HRMS BRUKER Daltonic equipped with an electrospray ionization source (GC-APCI). 1µL of diluted sample (20x in heptane) was injected in Split mode (x20) in the GC-TOFHRMS system, on a 30m long Restek RXi Sil-5MS column, 0.25mm internal diameter and 0.25µm film thickness. The temperature of the injector was 260°C. The carrier gas used was helium at a constant flow rate of 4.0 mL.min-1. The initial furnace temperature was set at 80°C for 1 minute followed by a 25°C per minute increase to 140°C, then a 20°C per minute increase to 200°C and finally a 15°C per minute increase to 310°C with a 5 min hold time. The mass spectrometer worked in Scan mode from 100 to 1000 m/z at 3 Hz. The temperature of the transfer capillary was 200°C and the corona needle at 1800 nA. Chromatograms and mass spectra are analyzed using Bruker's Compass Data Analysis V4.3 software.

Transesterification process
The transesterification reactions were carried out in two stages. During the first step, the fatty acids in vegetable oil were esterified by homogeneous acid catalysis using a 30:1 molar ethanol:oil ratio in the presence of concentrated H_2SO_4 (1% m/m of oil) and moderate agitation (250 rpm at 78°C/1 hour). Then, the reaction were neutralized with 25% (m/m oil) of a sodium bicarbonate solution for 5 min with slow stirring and the phases have been separated in a separatory funnel. The ester obtained was dried and then filtered afterwards with a mixture of anhydrous sodium sulphate (Na_2SO_4). The residual solvent was evaporated under reduced pressure and the ester-rich phase was then weighed. The unreacted triglycerides and the partial glycerides (mono- and di-glycerides) contained in the ester-rich phase were transesterified in second step. The reaction was continued by varying the ethanol : oil molar ratio (6 and 8), the concentration of the KOH catalyst 1.1% (m/m oil) and the temperature 60 °C for two (02) hours with moderate stirring (250 rpm). The final mixture was separated in a funnel separatory and the phase rich in esters was dried with anhydrous sodium sulfate and filtered on a filter paper.

Biodiesel-diesel blends

Some of the formulated biodiesel was used to prepare biodiesel-diesel blends. Thus, the blends were prepared at 20°C in an Erlenmeyer flask with a lid at a stirring speed of 250 rpm for 10 min. As part of our work, *Ceiba pentandra* ethyl biodiesel was blended with pure diesel in three proportions, namely 5%, 10% and 20% by volume, to evaluate its properties. These blends were named B5, B10 and B20 respectively.

High pressure density measurement

The density (ρ) was measured with an Anton Paar K.G. DMA 45 vibrating tube density meter as a function of pressure and temperature for unconventional vegetable oil, ethyl biodiesel and pure biodiesel-diesel blend. An additional cell DMA 512 has been adapted to this instrument, which can measure under pressure up to 40 MPa. In this study, the apparatus allowed us to perform measurements by varying the temperature from 293.15 to 353.15 K and the pressure from 0.1 to 40 MPa. The DMA 45 was connected to an mPDS 2000V3, allowing us to measure the vibration period with a high certain accuracy. A Julabo Polystat 36 thermostatted bath is used to control the temperature of the vibrating tube cell. The temperature is measured inside the cell by an AOIP thermometer PN 5207 with an uncertainty of 0.05 K. A volumetric piston pump is used to apply pressure to the system, which is measured by an HBM PE 200/2000 sensor with an uncertainty of 0.1 %. Before and after each handling (sample loading), the density meter and all capillaries are cleaned with petroleum hexane ether to remove any traces of residues of the previously investigated substance. Once this cleaning process is completed, a vacuum is applied to the system before introducing the sample to be studied. When thermal equilibrium is reached, the vibration period of the cell is determined at different pressures, starting with 0.1 MPa, followed by the highest pressures. Then the temperature of the liquid bath is changed and a new isotherm is studied.

In this type of device, the density is related to the period of vibration by the equation:

$$\rho(p, T) = A(p, T)\zeta^2(p, T) - B(p, T) \qquad (\text{Error! Bookmark not defined.})$$

With ρ (p, T) the density of the sample, ζ (p, T) the period of oscillation, A (p, T) and B (p, T) two characteristic parameters of the instrument.

As far as calibration is concerned, we have opted for the method used by Comuñas *et al.* (2008) which is more suitable for our field of investigation and is based on the hypotheses made by Lagourette et *al.* 1992[24,25].

Taking into account these hypotheses, the equation below can be written:

$$\rho(T, P) = \rho_{eau}(T, P) + \rho_{eau}(T ; 0,1MPa)\left[\frac{\zeta^2(T, P) - \zeta_{eau}^2(T, P)}{\zeta_{eau}^2(T ; 0,1MPa) - \zeta_{vide}^2(T, P)}\right] (\text{Error! Bookmark not defined.})$$

The estimated uncertainty of the measured pressure was ± 0.015 MPa (Presens Precise Gold Plus pressure transmitter) and the estimated uncertainty of the determined density was ± 0.5 kg m^{-3} (i.e., around 0.05% for density close to water density).

Kinematic Viscosity measurements

The kinematic viscosity of our samples was determined with a SCHOTT-GERÄTE Ubbelohde viscometer. A kinetic energy correction is applied depending on the diameter of the capillary tubes used. For this purpose, approximately 15 mL of the filtered sample was introduced into the reservoir (capillary tube). The maximum filling volume is limited by the markings on the reservoir. After filling, the viscometer is hung with its holder in a transparent thermostat from SCHOTT-GERÄTE. In order to avoid measuring errors of the viscometer, the temperature in the thermostat has been kept constant at ± 0.01°C. Each capillary tube is provided with a calibration certificate, but the calibration of the capillary viscometer was checked at several temperatures using "Viscosity Reference Standard" fluid S20 provided by ColeParmer. The uncertainty is less than 1%.

III. Result

The fatty acid ester composition of *Ceiba pentandra's* unconventional seed oil ethyl biodiesel was determined using a GC Scion 486 coupled to timsTOF HRMS BRUKER Daltonic equipped with an electrospray ionization source (GC-APCI). **Table no 1** shows the composition and calculated thermophysical properties of fatty acid ethyl esters from *Ceiba pentandra* seed oil shows the chromatogram and mass spectrum of fatty acid esters of ethyl biodiesel from this seed oil. As shown in the table (**Table no 1**), the formulated ethyl biodiesel ethyl derived from seed oil from *Ceiba pentandra* seeds contains 36.48% saturated fatty acid esters (SFA); 23.16% monounsaturated fatty acid esters (MUFA) and 40.35% polyunsaturated fatty acid esters (PUFA). The main constituents of the formulated ethyl biodiesel are palmitate (C16:0) esters (24.53%), oleate

(C18:1) (19.6%) and linoleate (C18:2) (36.92%). The thermophysical properties of ethyl esters of such as fatty acid: cetane number, kinematic viscosity, density and gross calorific value are shown in **Table no 1**. These values were estimated using equations **(1)** - **(4)**. As expected, cetane number, viscosity and gross calorific value increase with increasing molecular weight. Furthermore, it is noted that these properties decrease as the number of double bonds increases. On the other hand, the density increases as the molecular weight decreases and the degree of unsaturation increases.

Table no 1: Composition and calculated thermophysical properties of fatty acid ethyl esters from *Ceiba pentandra* seed oil

Ethyl esters	(%)	η (mm²/s) at 40°C	CN	Δ (MJ/kg)	ρ (g/cm³) at 20°C
Myristate (C14:0)	1,19	2,87	61,16	38,33	0,87
Palmitate (C16:0)	24,53	3,83	69,64	39,19	0,87
Stearate (C18:0)	5,96	4,96	78,11	39,88	0,86
Arachidate (C20:0)	0,52	6,27	86,58	40,45	0,86
Behenate (C22:0)	0,65	7,77	95,05	40,92	0,86
Eicosatrienoate (C23:0)	2,86	6,89	90,24	40,66	0,86
Lignocerate (C24:0)	0,77	9,47	103,52	41,32	0,86
Palmitoleate (C16:1)	0,63	3,14	49,03	38,93	0,88
Oléate (C18:1)	19,6	4,08	57,50	39,63	0,88
Gondoate (C20:1)	0,92	5,16	65,97	40,20	0,87
Nervonate (C24:1)	0,47	7,82	82,91	41,09	0,87
Erucate (C22:1)	1,54	6,41	74,44	40,68	0,87
Linoleate (C18:2)	36,92	3,35	36,89	39,37	0,89
Linolenate (C18:3)	2,50	2,75	16,28	39,12	0,90
Eicosatrienoate (C20:3)	0,93	3,49	24,61	39,70	0,90
SFA	36,48				
MUFA	23,16				
PUFA	40,35				

Total Saturated Fatty Acids: SFA; Total Monounsaturated Fatty Acids: MUFA; Total Polyunsaturated Fatty Acids: PUFA; Kinematic viscosity:η (mm²/s); Cetane number: CN;Higher Heating Value: Δ (MJ/kg) and Density: ρ (g/cm³).
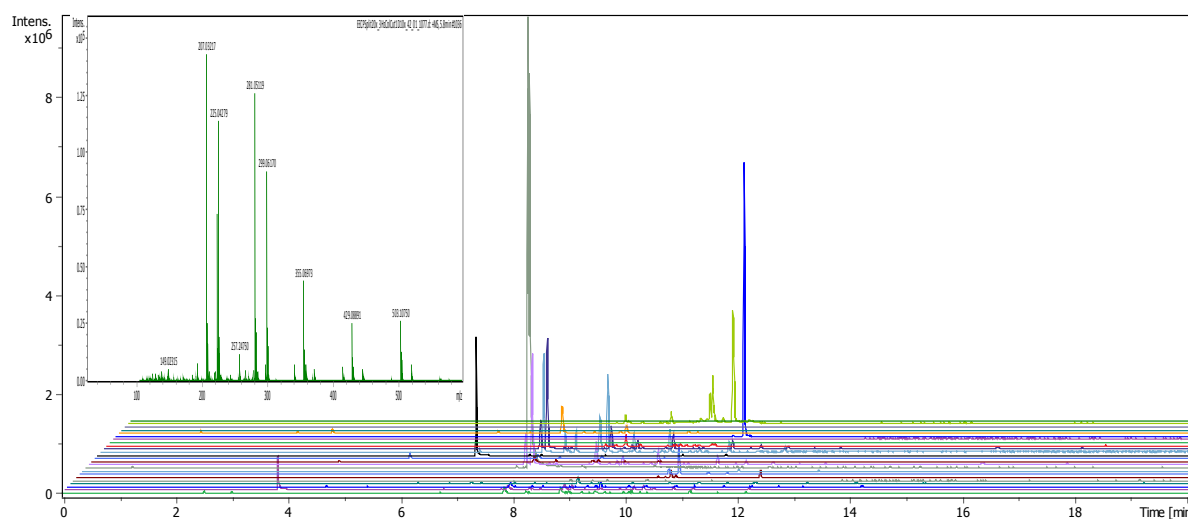
Some important properties were determined on biodiesel and on blends of biodiesel with pure diesel (**Table no 2**). Analysis of this table shows that the acid index values of biodiesel and biodiesel-pure diesel blends are all below the limit value set by the standards (max 0.5mg KOH/g). There is a progressive decrease in

the acid index value with the amount of biodiesel in the blend. These low acid index values obtained show a high oxidation stability and a longer shelf life during transport and storage. The decrease in the acid index of biodiesel may be due to the esterification reaction of free fatty acids to fatty acid ethyl esters during the transesterification process in acid homogeneous catalysis. The cetane number values of biodiesel as well as the 5%, 10% and 20% (v/v) volume blends of biodiesel with pure diesel are consistent with those recommended by ASTM D6751. In addition, cetane number values decrease and approach that of petroleum diesel depending on the proportion of ethyl biodiesel in the blends (B5, B10 and B20). In fact, a high cetane number for biodiesel shows better ignition quality with a shorter lag time than for fossil diesel. In addition, refractive index values for biodiesel and pure biodiesel-diesel blends range from 1.447 to 1.468.

Table no 2: Physical-chemical and fuels properties of biodiesel and biodiesel-diesel blends

| Properties	B5	B10	B20	B100	Normative methods	Limit values min	max
Acid index (mg KOH/g)	0.06 ±0.01	0.08±0.01	0.16±0.03	0.23±0.01	EN ISO 14214	-	0.5
Iodine Index (mg I_2/100g)	90.79±0.15	92.03±0.11	98.67±0.10	116.05±0.09	EN 14111	-	120
Cetane number (313.15K), (nD)	48.26±0.08	49.86±0.10	50.60±0.12	58.82±0.10	ASTM D6751	47	51
Pour point (°C)	-12	-8	-5,6	-2	ASTM D6751	-15	10
Flash point (°C)	87	106	128	156	ASTM D975	60	80
Kinematic viscosity (313.15K à 0.1MPa), ($mm^2.s^{-1}$)	2.82	3.07	3.80	5.37	EN ISO 14214	3.5	5.0
					ASTM D6751	1.9	6.0
Density (313.15K à 0.1MPa), ($Kg.m^{-3}$)	823.43	827.00	833.50	887.98	EN ISO 14214	860	900
Refractive index (293,15K), (nD)	1.447	1.456	1.457	1.468	-	-	-

Not determined = - and nD=not defined

The density of biodiesel and pure biodiesel-diesel blends with three concentrations of biodiesel (5%, 10% and 20%) was measured at different temperatures (293.15 ≤ T ≤ 353 K) as a function of pressure on the one hand. The experimental values are presented in **Table no 3**.Graphsshow the variation in density as a function of temperature and pressure. In general, it can be seen that density is a linear function of temperature and pressure for both ethyl biodiesel and blends. In addition, there is a linear variation in density with respect to the proportion of biodiesel in the blends.

Table no3: Density of biodiesel (B100) and biodiesel-diesel blends (B5, B10, B20) as a function of temperature (293.15 to 353.15) K and pressure (0.1 to 40) MPa

Pressure (MPa)	Density ($Kg.m^{-3}$) Temperature (K)			
	293.15	313.15	333.15	353.15
B100				
0.1	902.49	887.98	874.11	860.18
10	907.69	894.21	880.71	867.36
20	912.99	899.66	886.62	873.89
30	917.90	905.13	892.29	880.27
40	922.59	910.07	897.68	886.07
B5				
0.1	837.91	823.43	808.93	794.82
10	843.98	830.23	816.43	802.41
20	849.70	836.49	823.24	810.22
30	854.94	842.43	829.53	817.16
40	859.95	847.68	835.39	823.62
B10				

0.1		840.32	827.00	812.38	798.02
10		847.17	833.36	819.64	806.24
20		852.84	839.72	826.51	813.52
30		857.94	845.12	832.80	820.71
40		862.95	850.62	838.61	826.78
B20					
0.1		848.51	833.50	819.40	804.90
10		853.80	840.15	826.66	813.08
20		859.77	846.12	833.33	820.51
30		864.91	851.87	839.53	827.31
40		869.83	857.28	845.19	833.48
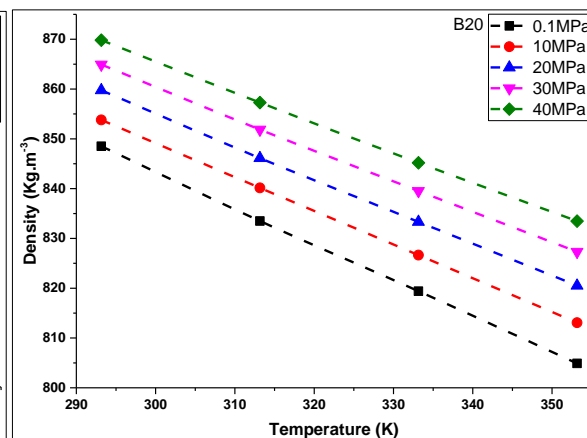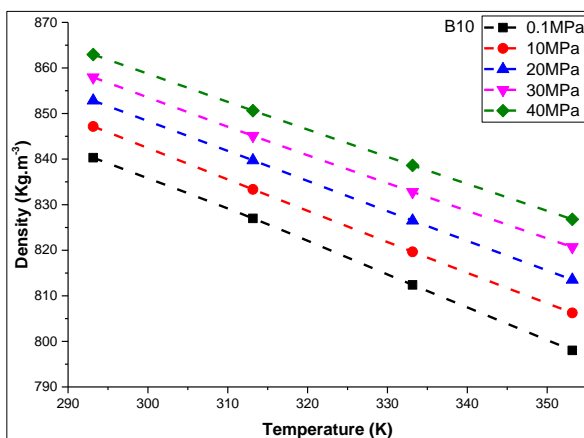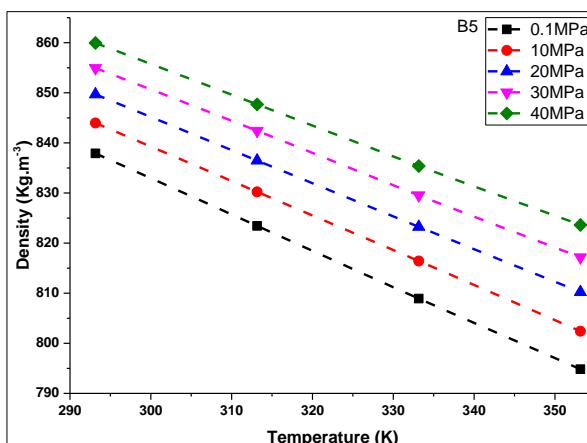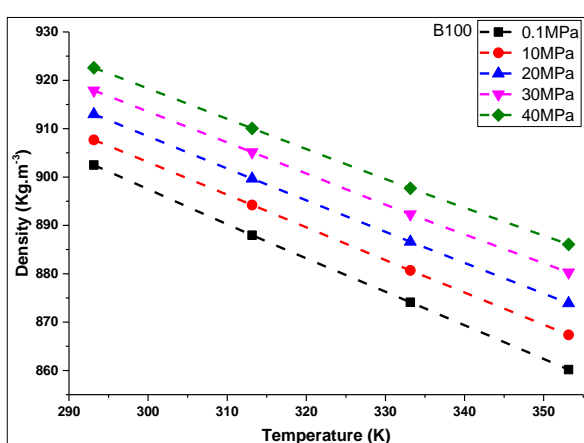
The density values of biodiesel and biodiesel-diesel blends of [298.15 - 353.15] K and pressures ranging from [0.1 - 40] MPa summarized in **Table no 3** were correlated using the TAIT-Like equation.

$$\rho(T, P) = \frac{\rho_0(T)}{1 - \rho_0 A \ln\left(1 + \left(\frac{P - P_0}{B(T)}\right)\right)} \quad (\text{Error! Bookmark not defined.})$$

With $\rho_0(T) = A_0 + A_1 T + A_2 T^2$ et $B(T) = B_0 + B_1 T + B_2 T^2$

The comparison of the experimental density values and those found with the TAIT-Like correlation was made using the absolute mean deviations (AAD), the maximum deviation (DMax) and the mean deviation (Bias). These AAD, DMax and Bias parameters were determined from the equations defined below[26]:

$$AAD = \frac{100}{N} \sum_{i=1}^{100} \left| \frac{\rho_i^{exp} - \rho_i^{calc}}{\rho_i^{exp}} \right|; \qquad (\text{Error! Bookmark not defined.})$$

$$DMax = Max\left(100 \left| \frac{\rho_i^{exp} - \rho_i^{calc}}{\rho_i^{exp}} \right|\right); \qquad (\text{Error! Bookmark not defined.})$$

$$Bias = \frac{100}{N} \sum_{i=i}^{N} \frac{\rho_i^{exp} - \rho_i^{calc}}{\rho_i^{exp}} \qquad (\text{Error! Bookmark not defined.})$$

With N the number of experimental data for each sample, ρ^{exp} and ρ^{cal} respectively the experimental density and the density obtained with equation **(7)**.

The parameters of the TAIT-Like equation as well as AAD, DMax and Bias determined with the density correlation are grouped in **Table no 4**.

Table no4: Parameters and deviation obtained from the TAIT-Like equation for density correlation and calculation of the isothermal compressibility coefficient

Coefficients	B5	B10	B20	B100
A_0 (g.cm^{-3})	1,6236	-0,0904	2,0053	1,1466
A_1 (g.cm^{-3}.K^{-1})	-0,0053	0,0097	-0,0094	-0,0009
A_2 (g.cm^{-3}.K^{-2})	$1,4179 \times 10^{-6}$	$-3,1653 \times 10^{-5}$	$2,6691 \times 10^{-5}$	4×10^{-6}
ρ_0 (g.cm^{-3}) à 293,15K	0,8379	0,8403	0,8485	0,9024
A (MPa)	-0,0825	-0,0950	-0,1028	-0,1108
B (MPa)	89,6024	102,0001	123,1022	163,2999
AAD (%)	0,0020	0,0025	0,0023	0,0068
DMax (%)	0,0044	0,0055	0,0057	1,9643
Bias (%)	0,0012	-0,0010	0,0005	0,2677

The mean absolute differences (AAD) between the density values measured and those calculated using equation **(7)** are equal to 0.0068% for ethyl biodiesel and less than 0.005% for biodiesel-diesel blends, demonstrating the good quality of the density modeling.

The coefficient of isothermal compressibility is one of the important properties for understanding the thermodynamic behavior of fluids in engines. Furthermore, it is one of the properties to be taken into account when selecting a hydraulic fluid for a particular application. Indeed, low compressibility translates into a fast response time, high transmission speed at high pressure and low power loss. In hydraulic systems operating at high pressure, oils with low compressibility are required to transmit power efficiently. Based on the density measurement results of formulated ethyl biodiesel and biodiesel-diesel blends presented above, we were able to calculate the isothermal compressibility χ_T as a function of pressure [0.1 to 40] MPa in the temperature range [15 to 353.15] K using the parameters of the TAIT-Like equation.

$$\chi_T = \left(\frac{1}{\rho}\right)\left(\frac{\partial \rho}{\partial P}\right)_T \qquad (\text{Error! Bookmark not defined.})$$

The product of the inverse of density **(7)** and its derivative with respect to pressure at constant temperature, allowed us to write:

$$\chi_T = \frac{A\,\rho_0(T)}{B(T) + P - P_0\left[1 - A\,\rho_0(T)\ln 1 + \left(\frac{P - P_0}{B(T)}\right)\right]} \qquad (\text{Error! Bookmark not defined.})$$

Isothermal compressibility coefficient values for ethyl biodiesel and 5%, 10% and 20% pure biodiesel-diesel blends are listed in **Table no 5**.

Table no5 : Coefficient of isothermal compressibility k_T (MPa^{-1}) of formulated biodiesel and of blends with diesel as a function of temperature and pressure.

Pressure (MPa)	10^3 K_T (MPa^{-1}) Temperature (K)			
	293.15	313.15	333.15	353.15
B100				

0.1	0.612	0.736	0.773	0.886
10	0.580	0.666	0.713	0.803
20	0.552	0.609	0.661	0.735
30	0.526	0.560	0.617	0.678
40	0.503	0.520	0.578	0.629
B5				
0.1	0.772	0.876	1.006	1.050
10	0.700	0.790	0.884	0.962
20	0.641	0.720	0.788	0.887
30	0.591	0.661	0.712	0.824
40	0.548	0.612	0.649	0.770
B10				
0.1	0.783	0.820	0.975	1.099
10	0.719	0.756	0.869	0.974
20	0.665	0.701	0.783	0.875
30	0.618	0.654	0.713	0.795
40	0.578	0.613	0.656	0.728
B20				
0.1	0.709	0.836	0.929	1.108
10	0.661	0.759	0.844	0.967
20	0.618	0.694	0.773	0.857
30	0.581	0.641	0.714	0.771
40	0.549	0.595	0.663	0.701

Graphs show the variation of isothermal compressibility of formulated ethyl biodiesel (B100) and those of biodiesel blends B5, B10 and B20 with diesel as a function of pressure at constant temperature. In general, the isothermal compressibilities of ethyl biodiesel derived from *Ceiba pentandra* unconventional seed oil and pure biodiesel-diesel blends decrease as pressure increases [0.1 to 40] MPa along the isotherms. On the other hand, these values of the coefficient of compressibility increase with temperature at constant pressure. Isothermal compressibility values evaluated range from $5.03 \cdot 10^{-4}$ MPa^{-1} at 293.15K to $8.86 \cdot 10^{-4}$ MPa^{-1} at 353.15K for ethyl biodiesel derived from *Ceiba pentandra* seed oil. On the other hand, those for pure biodiesel-diesel blends range from $5.48 \cdot 10^{-4}$ MPa^{-1} to 293.15 K and $1.05 \cdot 10^{-3}$ MPa^{-1} to 353.15 K, $5.78 \cdot 10^{-4}$ (293.15 K) and $1.09 \cdot 10^{-3}$ (353.15 K) and then $5.49 \cdot 10^{-4}$ (293.15 K) and $1.11 \cdot 10^{-3}$ (353.15 K) respectively for B5, B10 and B20.
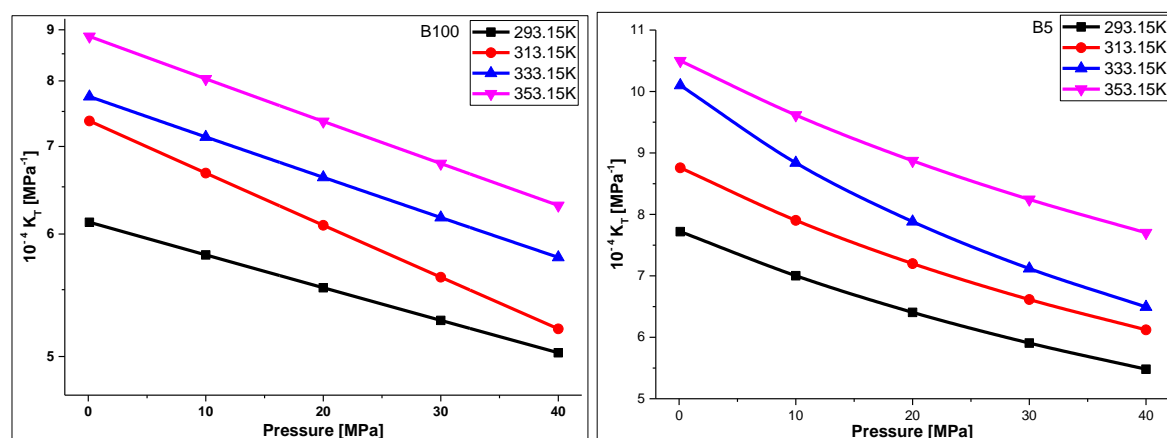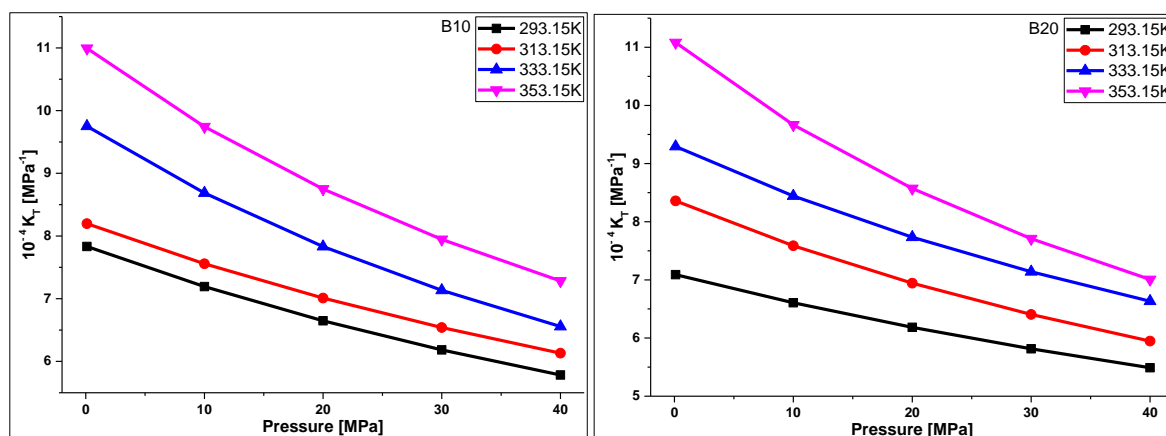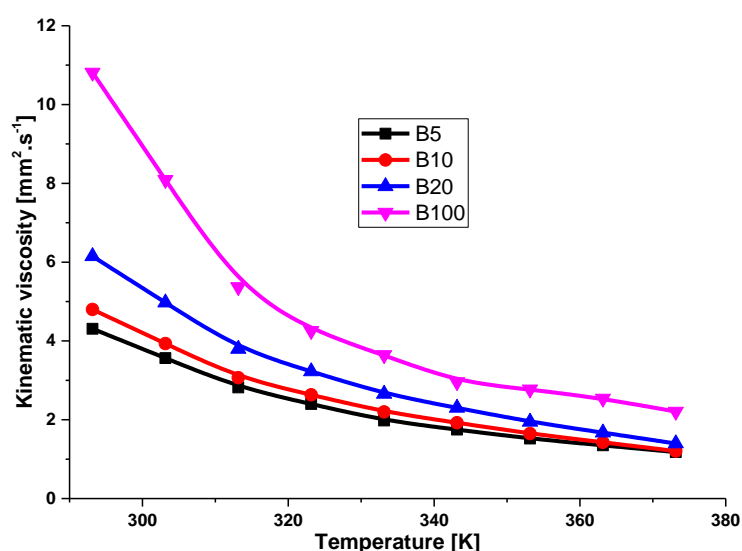
Kinematic viscosity measurements of formulated biodiesel and biodiesel-diesel blends

The kinematic viscosity of ethyl biodiesel and pure biodiesel-diesel blends was determined at atmospheric pressure and temperatures ranging from 293.15K to 373.15K. The data are presented in **Table no 6**.

Table no6 : Measurement of the kinematic viscosity of formulated ethyl biodiesel and blends of biodiesel with pure diesel as a function of temperature (293.15 to 373.15K)

Temperature [K]	B5	B10	B20	B100
293,15	4,31	4,80	6,15	10,81
303,15	3,56	3,93	4,97	8,09
313,15	2,82	3,07	3,80	5,37
323,15	2,40	2,63	3,23	4,26
333,15	1,98	2,20	2,66	3,14
343,15	1,75	1,92	2,30	2,96
353,15	1,52	1,65	1,95	2,77
363,15	1,35	1,43	1,67	2,14
373,15	1,18	1,21	1,40	1,51

As expected, the kinematic viscosity of ethyl biodiesel and blends decreases exponentially with increasing temperature. The kinematic viscosity of ethyl biodiesel is higher than that of pure biodiesel-diesel blends. However, the kinematic viscosity of ethyl biodiesel decreases with the proportion of ethyl biodiesel in the blends and with increasing temperature at atmospheric pressure.

IV. Discussion

The experimental results on fatty acid methyl esters (FAME) reported by Knothe are similar to those found in the present study for fatty acid ethyl esters (FAEEs)[27,17]. In addition, the thermophysical properties of FAMEs are found to be superior to those of FAMEs reported by Knothe[26]. These results show that thermophysical properties are influenced by molecular weight and number of double bonds in alkyl esters.

Kinematic viscosity is one of the very important fuel properties that is linked to diesel engine performance[28]. It characterizes the degree of fluidity and atomization of the fuel at low temperatures[29]. As shown in **Table no 1**, the kinematic viscosity of formulated biodiesel is comparable to that of pure diesel (ASTM D6751). However, the blends of biodiesel with pure diesel are all below the kinematic viscosity recommended by the U.S. standard (ASTM D6751). These kinematic viscosity values show that both formulated biodiesel and biodiesel-pure diesel blends can be used directly in conventional diesel engines without any major modifications. Another crucial property of biodiesel that also influences engine performance is density. As shown in **Table no 2**, the density values measured at 313.15 K are all in accordance with the standard (EN ISO 14214). These density values confirm the evaluated kinematic viscosity values. The pour point represents the tendency of the fuel to solidify at low temperatures. In addition, it should be noted that at low temperatures, biodiesel can solidify, causing the engine to shut down[30]. Therefore, it is necessary to know the lowest temperature at which ethyl biodiesel can be used as diesel in engines. Thus, the cold flow characteristic that represents the pour point of formulated biodiesel is 2°C. This value complies with ASTM D6751 specifications. However, the pour point values for blends of biodiesel with pure diesel are lower than those for formulated biodiesel and are consistent with those set by ASTM D6751 and ASTM D975. The self-ignition temperature (flash point) of formulated ethyl biodiesel is much higher than that of petrodiesel as specified by ASTM D975[31]. Moreover, this flash point value is comparable to that of biodiesels formulated from unconventional *C. oleifera*[32] and *Ceiba pentandra* seeds oils[33]. Therefore, the self-ignition temperature of the prepared ethyl biodiesel suggests more appropriate handling and storage of this biodiesel at a high temperature.

The density variation of biodiesel derived from seed oil from *Ceiba pentandra* and biodiesel/pure diesel blends is similar to the results reported in 2011 by Payri *et al.* for lubricant (Repsol Elite) and rapeseed methyl ester[34]. In sum, the evolution of density as a function of temperature and pressure in this present work corroborates the work in the literature[35,36]. As expected, it increases when the pressure rises, and decreases when the temperature rises. In addition, in hydrostatic applications, the density of oils is usually measured at 15°C, but the density is dependent on temperature and pressure because the volume of a fluid increases with temperature causing the density change.

Previous work shows similar values for methyl esters of rapeseed seed oil[37]. In addition, the isothermal compressibility values of formulated biodiesel are lower than those of B5, B10, B20 blends. For blends,

isothermal compressibility values decrease as the amount of biodiesel in the blend increases. These results are consistent with data from the literature[38, 39].

Ivaniš et *al.* (2016) reported similar results for biodiesels derived from vegetable oils from Sunflower, Soybean[40]. Benjumea et *al.* (2008) measured the kinematic viscosity of biodiesel and palm oil blends at different temperatures (289-373 K) and at five biodiesel concentrations (B0, B5, B20, B100). The authors found a linear variation in kinematic viscosity with respect to the proportion of biodiesel in the blends at a given temperature[41].

V. Conclusion

This study was conducted to determine the physico-chemical and fuel properties of ethyl biodiesel derived from the unconventional seed oil of *Ceiba pentandra* as well as blends prepared with biodiesel concentrations of 5%, 10% and 20%. The main constituents of the formulated ethyl biodiesel are palmitate (C16:0) esters (24.53%), oleate (C18:1) (19.6%) and linoleate (C18:2) (36.92%). An Anton Paar vibrating tube density meter was used to measure the density of our samples by varying the temperature (293.15-353.15) K and pressure (0.1- 40) MPa. A SCHOTT-GERÄTE Ubbelohde viscometer was also used to evaluate the effect of temperature on the kinematic viscosity of the samples at atmospheric pressure. In all cases, the density and kinematic viscosity of ethyl biodiesel and its blends decrease as the temperature increases; and both increase as the amount of biodiesel in the blends increases. All of the fuel properties of formulated ethyl biodiesel comply with U.S. (ASTM) and European (EN) standards. In addition, pure biodiesel-diesel blends (B5, B10 and B20) have shown very satisfactory results compared to ethyl biodiesel. Of all these encouraging results, *Ceiba pentandra* seed oil ethyl biodiesel and pure biodiesel-diesel blends can be used as a substitute for pure diesel in any modification. Isothermal compressibility increases with temperature at constant pressure and decreases as pressure increases along the isotherm (293.15-353.15) K. The values for the coefficient of isothermal compressibility reported for ethyl biodiesel are slightly lower than those for pure biodiesel-diesel blends.

Acknowledgements

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