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EXPERIMENTAL DETERMINATION OF FLAMMABILITY LIMITS OF FARNESANE, JET FUEL AND MIXES AT ATMOSPHERIC PRESSURE IN AIR

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Abstract. *The creation of alternative fuels for the aeronautical sector generates a need to know the safety properties of the same, among them is the flammability limits. The aim of this manuscript is to experimentally determine the flammability limits of Farnesane, Jet Fuel and mixtures of 10% (F10) and 50% (F50) in mass of Farnesane at atmospheric pressure with temperature variation. For this purpose, an experimental bench was built according to ASTM E681, in which the flame propagation is analyzed visually and contains a flask of 20.716L of borosilicate glass. A total of 161 tests were performed and the flammability limits of the samples were determined at atmospheric pressure and temperature ranging between 140 and 210 ° C, the results are compared with the scientific literature in order to validate the experiments. Prediction equations are proposed in this paper and for the lower flammability limit was an average absolute relative errors of 1,17% for Farnesane, 1,18 % for Jet Fuel, 0,715% for F50 and 2,84% for F10. For the upper flammability limit was an absolute relative errors of 1,16% for Farnesane, 0,62 % for Jet Fuel, 2,64% for F50 and 2,15% for F10.The absolute relative error shows good accuracy to the prediction porpoise for this paper specifically to this fuels.*

Keywords: *Farnesane, flammability limits, ASTM E681, combustion, termodynamics*

1. INTRODUCTION

The global aviation industry basically uses fossil fuels that account for 2-3% of global carbon dioxide emissions. As there is increasing demand for air transportation and greater concern for the environment, alternative fuels with low carbon emissions have become attractive. Therefore, it is necessary to conduct studies on their safety and behavior (Blakey *et. al.*, 2010).

Gutiérrez-Antonio *et. al.*, 2017, conducted a paper to review scientific and technological advances on the production process of renewable jet fuel and identify those that could lead to future implementation of a sustainable production chain. The pathway adopted to produce renewable jet fuel influences product composition, fuel cost, fuel properties, availability and environmental impacts. The pathways were shown in Figure 1. This work uses a renewable jet fuel called Farnesane produced by DSHC.

Liquid or gaseous fuels are commonly used in industrial procedures, thus it is necessary to be sure whether there is the risk of explosions under operating conditions or not. Flammability limits are a fundamental property for predicting possible explosions and designing protection systems.

In 2012, Coronado *et. al*., conducted a literature review on flammability limits with emphasis on ethanol in aeronautical applications by organizing theoretical and practical concepts on the matter. In 2014, Coronado *et. al*., determined the flammability limits of anhydrous and hydrous ethanol for aeronautical applications, and concluded that the water contained in hydrous ethanol acts as an inert substance and causes change, mainly in Upper Flammability Limits.

Mendiburu *et. al*., (2015) estimates lower flammability limits of C-H compounds in air at standard atmospheric pressure by using 120 C-H compounds and correlating a prediction formula for LFLs with low absolute error. Mendiburu *et. al*., (2016) also studies the effect of initial temperature on lower flammability limits of C-H-O compounds and concluded that adiabatic flame temperature cannot always be considered constant

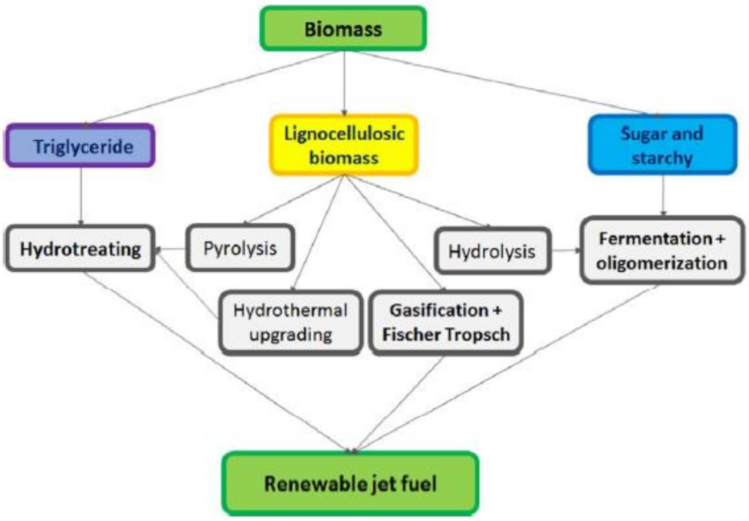

Figure 1: Pathways for the production of biojet fuel (Gutiérrez-Antonio et, al., 2017)

2. MATERIALS AND METHODOLOGY

First is presented the materials used in this work in which they include: Farnesane, jet fuel and the experimental bench. The methodology is developed as follows: at first, it is calculated the minimum and maximum volume of fuel required to be introduced into the heat chamber flask at standard atmospheric pressure and 25 ° C so as to become flammable with the air present in the flask, and then an experimental study is validated by making a comparison with literature data as regards atmospheric pressure, as well. Afterwards, once the flammability limits are determined as a function of temperature, they are converted into volume percentage.

2.1 Fuels

Farnesane is produced by Amyris through the DSHC, which is an industrial biotechnology company whose operation plant is located in Brotas, SP, Brazil. This biofuel is a mixture of paraffinic hydrocarbons with the empirical formula $C_{15}H_{32}$. It is a transparent liquid used for producing a sulfur-free fuel. After fermenting the sugarcane syrup, Farnesene, which is one of the intermediate products that have been widely used in various industrial segments, undergoes processes of distillation and hydrogenation, thus producing Farnesane.

Farnesane is a versatile alternative fuel that cannot only be used in conventional internal combustion engines, but also in the aviation industry, once mixed with traditional fuels. There are few works on Farnesane and its mixtures with jet fuel and aviation gasoline, thus this study is of paramount importance for the aeronautical industry.

Among the articles published for Farnesene or Farnesane, the following works stand out. George *et. al.,* (2015) study Farnesene concluding that its structure is attractive for chemical applications such as solvent. Chuck and Donnely (2014) tested the compatibility of new biofuels with Jet Fuel and conclude that Farnesene is very viscous for use in aeronautical turbines.

Carvalho (2014) studies the application of Farnesane in diesel engines and concludes that it transmits satisfactory power. Millo *et. al.,* (2014) studies the emission of a mixture of 30% of Farnesane in a diesel engine, concluding that the emission of CO decreases in medium and low loads. Ritcher *et. al.,* (2018) studies the combustion characteristics of Farnesane, concluding that it has similar combustion behavior to Jet Fuel.

Farnesane is a sulfur-free fuel which reduces the formation of soot, so Farnesane is one of the most promising biofuels today for reducing CO2 emissions in the aircraft industry.

Jet Fuel A1 in Brazil is known as QAV-1 whose internal identification is BR0030. It consists of 70 to 72% of paraffinic hydrocarbons, 20% of aromatic hydrocarbons, 5% of olefinic hydrocarbons and approximately 3% of sulfur, nitrogen and oxygenated compounds.

2.2 Experimental Bench

The experimental bench contains a flammability chamber, which has been built by meeting American Standard ASTM E681 with a few pertinent modifications to conduct experiments at reduced pressures. In addition to the chamber, the bench has devices that measure operating variables and three systems: the control, gas supply, data acquisition and monitoring systems.

It is heated through electric elements, its temperature can reach up to 300°C, it has a thermal isolation and an observation window with the purpose of filming flame structure, with a high-speed camera. The chamber also has a 20.716 L spherical flask that can be seen in Fig. 2. It was opted to use increased volume than that specified by ASTM E681 since there is no rule for high temperature and low pressures, which require less air and fuel. Further details about the test bench can be found in works published by Coronado *et. al*., 2012, 2014 and Quintero, 2013.

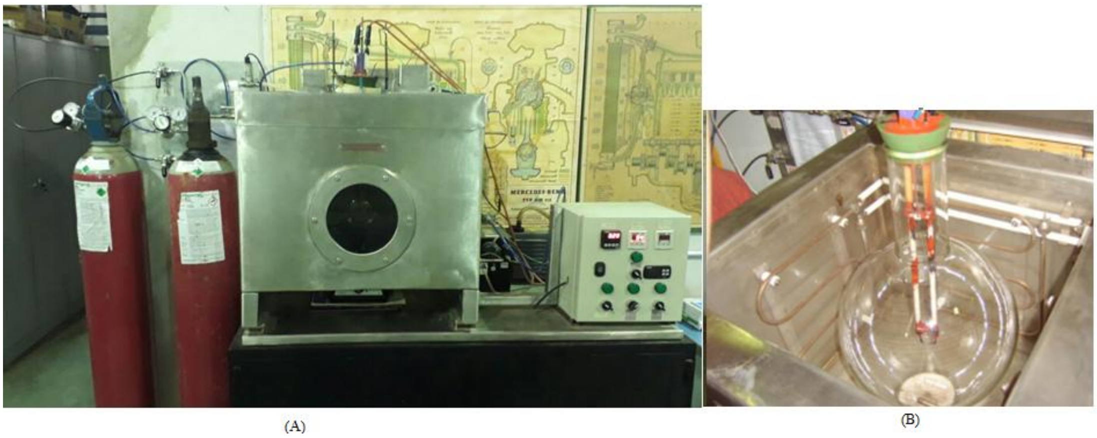

Figure 2: Flammabillity apparatus: A –Flammability Chamber, B – spherical flask of 20.716L

2.3 Fuel volume calculation

The formula of Farnesane is $C_{15}H_{32}$. The stoichiometric combustion reaction is given by Eq 1.

$$C_{15}H_{32} + 23(O_2 + 3.76N_2) \rightarrow 15CO_2 + 16H_2O + 56.4N_2 \quad (1)$$

In the Farnesane safety data sheet, it can be observed that its LFL is 0.48% and the UFL is 7,0% in volume at 25 ° C and 1 atm. Therefore, it is possible to obtain the number of moles through the flammability limits of Farnesane, as shown in Eq. 2:

$$\frac{n_{LFL/UFL}}{n_{LFL/UFL} + (n_{reag} - n_{Far})} = LFL/UFL \quad (2)$$

By using the ideal gases equation, it is obtained (Eq. 3):

$$n = \frac{PV}{RT} \quad (3)$$

On the other hand, the flask volume is 20,716 liters at 25 ° C and atmospheric pressure (101,325 kPa), where R is 8.314 [L.kPa.K-1.mol-1]. In order to calculate the minimum and maximum number of moles at 20.716 L, a ratio is calculated from the combustion reaction, as shown in Eq. 4

$$\frac{n}{n_{LFL/UFL} + (n_{reag} - n_{Far})} = \frac{y}{n_{LFL/UFL}} \quad (4)$$

Where: y is the minimum number of moles of Farnesane in 20,716 L. The minimum mass of Farnesane to form a flammable mixture respectively in the test vessel would be:

$$w_{min/max} = MW_{Far} * y \tag{5}$$

The specific mass of Farnesane is 770 kg/m^3. Therefore, the minimum volume to form a flammable mixture with Farnesane is presented in Eq. 6:

$$v_{min/max} = \frac{w_{min/max}}{\rho_{Far}} \tag{6}$$

As for temperature variation, Zabetaski (1965) is used for paraffinic hydrocarbons, which calculates the ratio between lower flammability limits and standard atmospheric pressure.

$$LFL_T = LFL_{298K}(1 - 0.00078(T - 25)) \tag{7}$$

$$UFL_T = UFL_{298K}(1 + 0.000721(T - 25)) \tag{8}$$

The LFL of mixtures at 25 ° C and 1 atm is calculated by Le Chatelier's Law for other fuels and mixtures, whose calculation is analogous to the example

2.4 Correction of Flammability Limits Into Percentage Terms From Experimental Results

The correction of LFL into percentage terms is given by Eq. 9.

$$LFL/UFL = \frac{v\rho}{MW}\frac{1}{\left(\frac{V}{22.4}\right)\left(\frac{p}{p_0}\right)\left(\frac{T_0}{T}\right)} x100\% \tag{9}$$

Where: v is the sample volume in cm^3; ρ is the sample specific mass in g / cm^3; MW is the fuel molar mass in g/mol; p is the test pressure in mmHg, T is the initial temperature, K; p_0 is standard atmospheric pressure and T_0 is standard temperature.

3. RESULTS AND DISCUSSION

A total of 161 tests have been performed at standard atmospheric pressure, whose results are satisfactory, but practical curves have a different slope than those obtained by the theoretical model. Some tests were carried out at temperatures ranging between 100 and 110 ° C, but there was no total evaporation of Farnesane and, therefore, the other tests were performed from an initial temperature of 140 ° C so as to ensure that Farnesane is completely evaporated.

For LII, combustion is complete because there is more air than fuel in the oxidant/fuel mixture, which makes the flame bluish. In the tests performed there was a loud noise and the expulsion of the bottle cap occurred. A 1 mL hypodermic syringe with a 0.02 mL scale was used for the tests, so the resolution of the measurement is ± 0.01 mL. The LII will be compared with the theoretical curves proposed by Zabestaski (1965) and Mendiburu *et. al.*, (2015).

On the other hand for LSI, combustion is incomplete, as it has more fuel than air in the oxidant/fuel mixture, making the flame orange. An interesting detail worth noting is test N° 636 performed at a temperature of 197 ° C and with a volume of 8 mL, before the standard ignition occurred, the autoignition of Farnesane occurred. So the tests of the upper flammability limits of Farnesane were limited to a temperature of 190 ° C. The resolution of the volume measurements inserted into the flask is ± 0.1 mL. The LSI will be compared with the theoretical curve proposed by Zabestaski (1965). At the LFL the graph curves are on top of each other because of the graph scale.

Figure 3-6 shows the flammability limits for the fuels tested and the theoretical curves cited above. Table 1 and 2 show the volume inserted in each test for LFL and UFL, respectively.

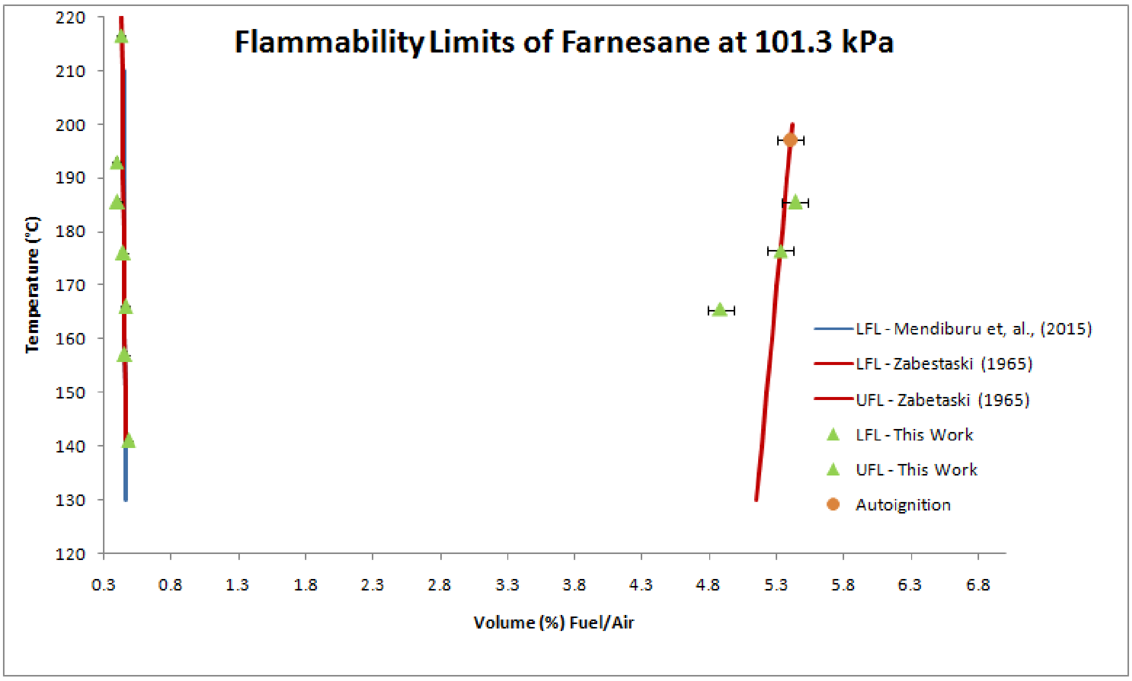

Figure 3: Flammability Limits of Farnesane at 101.3 kPa

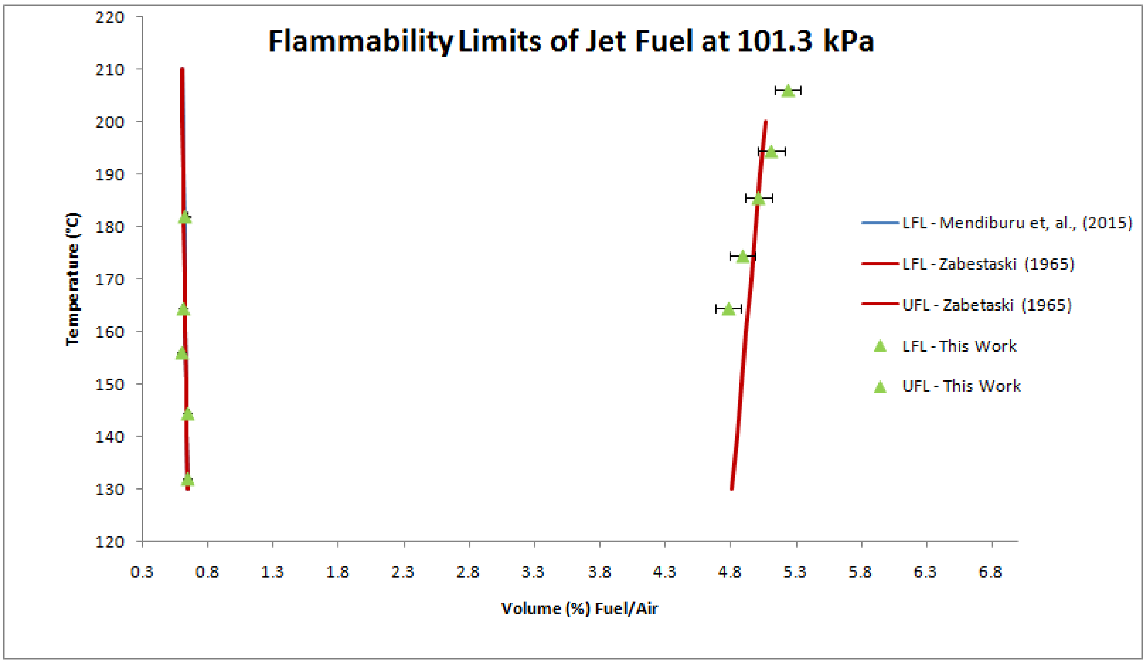

Figure 4: Flammability Limits of Jet Fuel at 101.3 kPa

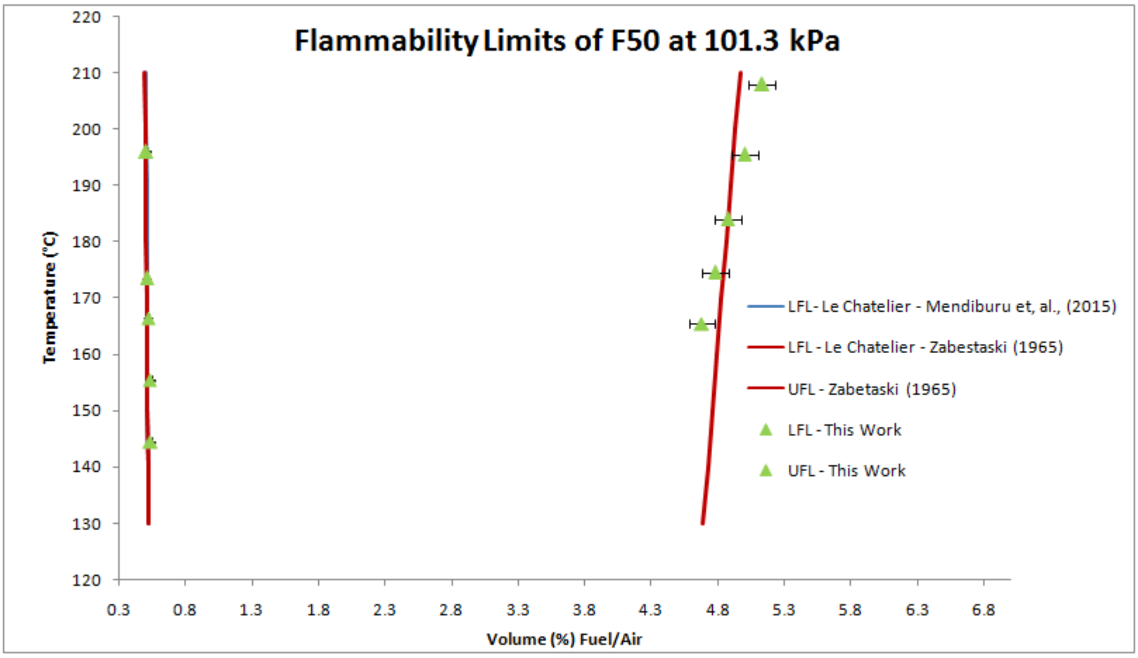

Figure 5: Flammability Limits of F50 at 101.3 kPa

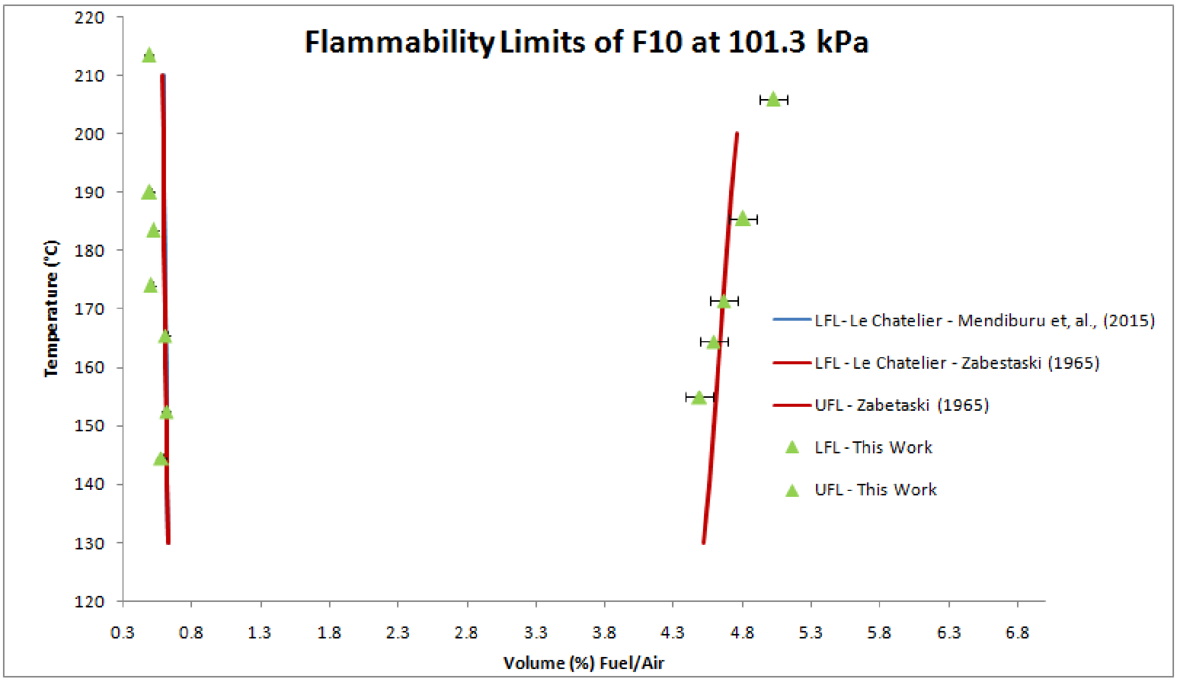

Figure 6: Flammability Limits of F10 at 101.3 kPa

Table 1: Raw Data for LFL

Exp. No.	**Volume (mL)**				Exp. No.
Farnesane – 101.3 kPa					
	T(°C)	Flame	No Flame	T(°C)	
5	156	0.78	0.7	158	4
6	173	0.94	0.64	172	37
7	175	0.86	0.52	218	60
8	172	0.77	0.58	217	61
62	216	0.64	0.7	164	321
320	168	0.76			
F50 – 101.3 kPa					
	T(°C)	Flame	No Flame	T(°C)	
11	156	0.76	0.7	156	12
38	172	0.7	0.64	175	39
55	194	0.66	1	109	48
187	146	0.78	1.1	114	49
322	166	0.72	0.6	192	56
			0.72	143	188
			0.66	144	189
			0.66	167	323
F10 – 101.3 kPa					
	T(°C)	Flame	No Flame	T(°C)	
50	174	0.58	0.54	174	40
52	191	0.56	0.5	173	51
59	215	0.52	0.44	190	53
324	166	0.62	0.5	189	54
327	183	0.6	0.48	212	63
			0.56	164	325
			0.54	184	326
Jet Fuel – 101.3 kPa					
	T(°C)	Flame	No Flame	T(°C)	
361	165	0.7	0.64	164	362
374	133	0.8	0.72	131	375
381	146	0.78	0.7	143	382
388	184	0.68	0.64	180	387

Table 2: Raw Data for UFL. Detail for test No. 636 where autoignition occurred.

Exp. No.		**Volume (mL)**			Exp. No.
		Farnesane – 101.3 kPa			
	T(°C)	Flame	No Flame	T(°C)	
550	175	8	9	176	554
584	185	8	8.5	177	555
601	166	7.5	8	165	579
			8.5	186	618
636	**197**	**8**			
		F50 – 101.3 kPa			
	T(°C)	Flame	No Flame	T(°C)	
346	157	6.5	7	156	345
414	166	6	7	163	412
460	174	6	6.5	165	413
493	185	6	6.5	175	460
514	196	6	6.5	184	494
599	207	6	6.5	195	515
			6.5	209	600
		F10 – 101.3 kPa			
	T(°C)	Flame	No Flame	T(°C)	
344	155	5	5.5	155	343
415	164	5	5.5	165	416
464	172	5	5.5	171	465
482	185	5	5.5	183	483
597	205	5	5.5	207	598
		Jet Fuel – 101.3 kPa			
	T(°C)	Flame	No Flame	T(°C)	
411	164	5	5.5	165	408
463	173	4.5	5.9	164	409
495	185	4.5	5.5	185	497
496	186	5	5.5	195	517
516	194	5	5.5	174	615
614	175	5	5.5	205	629
630	207	5			

At atmospheric pressure it is possible to correlate the equation 10 to determine the LFL and equation 11 to UFL of each sample used, so this work proposes the following modification of the equation presented by Zabetaski (1965) for paraffins, as follows.

$$LFL_T = LFL_{298K}(a - b(T - 25)) \tag{10}$$

$$UFL_T = UFL_{298K}(c + d(T - 25)) \tag{11}$$

Where coefficients a,b,c and d were calculated by least squares methods and T is in °C. Therefore, table 3 shows the coefficients a,b,c and d for for Farnesane, Jet Fuel, mixtures F50 and F10 respectively at standard atmospheric pressure.

Table 3: Coefficients of prediction equations

Fuel	a	b	c	d
Farnesane	1.104	0.00117	0.089	0.00435
Jet Fuel	1.086	0.00143	0.647	0.00217
F50	1.034	0.00108	0.527	0.000177
F10	1.14	0.00244	0.598	0.002

To test the accuracy of the predictions proposed by this paper its use the equation of Montgomery (2001) for the average absolute relative error (AARE), equation 12. Table 4 and 5 shows the absolute mean errors for LII and LSI respectively .

$$AARE = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|FL_{\exp} - FL_{prediction}\right|}{FL_{\exp}} * 100\% \qquad (12)$$

Table 4: Average absolute relative error – LFL

	Fuel			
	Farnesane	Jet Fuel	F50	F10
This Work	1.17 %	1.88 %	0.715 %	2.84 %
Mendiburu *et. al.*,(2015)	2.33 %	6.41 %	2.23 %	17.18 %
Zabetaski (1965)	1.62 %	1.29 %	2.02 %	16.48%

Table 5: Average absolute relative error – UFL

	Fuel			
	Farnesane	Jet Fuel	F50	F10
This Work	1.16 %	0.62 %	2.64 %	2.15 %
Zabetaski (1965)	3.19 %	1.8 %	1.84 %	2.13 %

For LFL the AARE are low for all theoretical equations, except F10 for the equations of Mendiburu *et. al.,* (2015) and Zabetaski (1965), since the points were displaced in relation to them. For the UFL, because it occurs an incomplete combustion, it is difficult to predict the products of the combustion, which makes the LSI more difficult to predict,but the AARE for the teorical equation was low too. The AARE for been low show good acuracy of the tests performed.

4. CONCLUSION

It has been determined the flammability limits of Farnesane (alternative aviation fuel), Jet Fuel at standard atmospheric pressure through a specially built experimental bench. Farnesane has lower LFL than Jet fuel and higher UFL. Farnesane have limits of flammability wider than jet fuel. Prediction equations are proposed in this paper and for the lower flammability limit was an average absolute relative errors of 1,17% for Farnesane, 1,18 % for Jet Fuel, 0,715% for F50 and 2,84% for F10. For the upper flammability limit was an absolute relative errors of 1,16% for Farnesane, 0,62 % for Jet Fuel, 2,64% for F50 and 2,15% for F10.The average absolute relative error shows good accuracy to the prediction for this paper specifically to this fuels.

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6. REFERENCE

Blakey, S., Rye L. And Wilson W. Christopher, 2010. "*Aviation gas turbine alternative fuels: A review"*. Proceedings of the Combustion Institute, v. 33, n. 2, p.2863-2885.

Gutiérrez-Antonio C., Gómez-Castro F.I., Lira-Flores J.A. De, Hernández S. , 2017. "*A review on the production processes of renewable jet fuel"*. Renewable and Sustainable Energy Reviews, v. 79, p. 709-729.

Christian J.R. Coronado, João A. Carvalho Jr., José C. Andrade, Ely V. Cortez,Felipe S. Carvalho, José C. Santos, Andrés Z. Mendiburu, 2012. "*Flammability limits: A review with emphasis on ethanol for aeronautical applications and description of the experimental procedure*". Journal of Hazards Materials, v. 241-242, p.32-54.

Christian J.R. Coronado, João A. Carvalho Jr, José C. Andradec, Andrés Z. Mendiburu, Ely V. Cortez, Felipe S. Carvalho, Beatriz Gonc¸ alves, Juan C. Quintero, Elkin I. Gutiérrez Velásquez, Marcos H. Silva, José C. Santos, Marco. A.R. Nascimento, 2014. *"Flammability limits of hydrated and anhydrous ethanol at reduced pressures in aeronautical applications*". Journal of Hazards Materials, v. 280, p.174-184.

Andrés Z. Mendiburu, João A. de Carvalho Jr, Christian R. Coronado, 2015. *“Estimation of lower flammability limits of C H compounds in air atatmospheric pressure, evaluation of temperature dependence an ddiluent effect”*. Journal of Hazards Materials, v. 285, p.409-418.

Carvalho A. L. V. *Desempenho e Emissões de Gases de um Mci-Diesel Utilizando Óleo Diesel E Mistura De Biocombustível*. Dissertação (Mestrado em Engenharia Energia) – Departamento de Ciências Térmicas, Universidade Federal de São João Del Rei, São João Del Rei, 2014.

Chuck C. J., Donnelly J., 2014. *The compatibility of potential bioderived fuels with Jet A-1 aviation kerosene*. Applied Energy, v. 118, p.83-91, 2014.

George K. W., Alonso-Gutierrez J., Keasling J. D., Lee T. S. *Isoprenoid Drugs, Biofuels, and Chemicals—Artemisinin, Farnesene, and Beyond*. Advances in Biochemical Engineering/ Biotechnology, v. 148, p. 355, 2015

Millo F., Bensaid S., Fino D., Marcano S. J. C., Vlachos T., Debnath, B. K. *Influence on the performance and emissions of an automotive Euro 5diesel engine fueled with F30 from Farnesane*. Fuel, v. 138, p. 134-142, 2014.

Montgomery D.C, 2001. *Desing and Analysis of Experiment*. Fifth ed., John Wiley & Sons, New York.

PETROBRAS DISTRIBUIDORA S.A. Ficha de Informação de Segurança de Produto Químico – FISPQ BR0030, QAV-1, 2014.

Quintero J.G.C., 2013.“*Experimental determination and prediction of the limits of flammability of ethanol anhydrous and hydrated for use in aircraft industry*”. Dissertation (Masters Degree in Energy Conversion) (in Portuguese), Federal University of Itajubá–UNIFEI, Mechanical Engineering Institute–IEM, Itajubá, MG, Brazil, p. 169.

Richter S., Kathrotia T., Naumann C., Kick T., Slavinskaya N., Braun-Unkhoff M., Riedel U. *Experimental and modeling study of farnesane***.** Fuel, v. 215, p. 22-29, 2018.

Zabetakis G. M., 1965. “*Flammability Characteristics of Combustible Gases and Vapors”*. US Bureau of Mines Bulletin, United States Government Printing Office, Washington. v. 627, p. 113.

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