Predictive Model for the Fluidity of Jet Fuel-Biofuel Mixtures for Aviation

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The increase in GHG in the atmosphere, which causes global warming, has promoted the implementation of biofuels in all energy sectors, including the aviation industry. Because according to Kroyan et al. (2022), in 2019, 363 billion liters of fossil fuel for aircraft were used on commercial flights, reaching a peak of emissions before the pandemic in 2019 of 1027 Mt CO_2 eq, (Ballal et al., 2023), generating the need to mitigate this value. For this reason, the International Air Transport Association (IATA) has established the goal of reaching zero net emissions by 2050, supporting the use of sustainable fuels (Roca, 2022).

1. Introduction

In contribution to the preceding, efforts have been deepened in worldwide studies on the production of biofuel for aviation starting from biomass, as well as the implementation of mixtures composed of fossil and renewable fuels, which comply with the standards of the D-1655 standard. of ASTM and contribute to reducing CO_2 emissions, one of the gases with the greatest environmental impact. In the study by Mayorga et al. (2020), the production of biodiesel (FAME) was carried out at bank scale from palm kernel oil by transesterification; followed this, the transesterification reaction of palm kernel oil was studied to produce Biodiesel FAME, using KOH as a catalyst (Mayorga et al., 2020). Then a series of mixtures were carried out with conventional aviation fuel (Jet A-1) and biodiesel derived from palm and palm kernel oil, to which the fluidity properties were evaluated, focusing on the freezing point, using as a method of analysis, the ASTM standard D-2386-18 was obtained as a result that one of the main drawbacks of the aeronautical industry when incorporating biofuels is that there is an instability of these at low temperatures (Mayorga et al., 2021). These biofuels and bioethanol from sugarcane have been tested in blends up to 20% on a ground test bench for the J69 turbine at the CAMAN air base of the Colombian Air Force (FAC) in Madrid, Colombia.The initiative has been taken to carry out a series of mixtures of Jet A-1 with biofuels (mainly based on palm and palm kernel oil, and in addition, anhydrous alcohol was used) in order to evaluate and analyse one of the properties of freezing point. Since there is little information in the literature on the L-S (Liquid-Solid) equilibrium for the systems studied, it is necessary to apply a model to predict this property, and validate its effectiveness in this task using the experimental values.
Since there is little information in the literature on the liquid-solid equilibrium for the studied systems, a predictive model is required to guide the evaluation of these mixtures. Several authors have developed models to predict the freezing point of multicomponent mixtures using equations of state to determine the activity coefficients of both the liquid and solid phases, as in the case of SRK (Soave Redlich Kwong) (Bowen et al., 2022). In this work, an ideal model will be approached as a preliminary approximation considering a binary mixture. The main objective is to qualify and identify which blends meet the ASTM requirement (less than or equal to -47 °C) (ASTM standard D-1655).

2. Methodology

The methodological development is divided into two stages for determining the point of mixtures between 5 and 20% by biofuel volume with Jet Fuel A1: the experimental part and the predictive part of the selected model. Once the model has been built, the freezing and melting curves are simulated for each of the three mixtures in order to make a comparison with the experimental values according to the proportions used.

2.1 Experimental

For the experimental tests, 3 types of biofuels were used (ethanol, FAME biodiesel from palm oil, and FAME biodiesel from palm kernel oil), which were mixed with Jet Fuel in the following 4 proportions (by volume): 5%, 10%, 15% and 20%, so a total of 12 samples were generated. In preparing these mixtures, the respective amounts of each of the two components were measured by mass of the Traveler Ohaus - TA501 analytical balance to reduce the error in volume measurement. The mixtures were formulated following the principles of additivation in order to be as homogeneous as possible, mainly through one, that is, from the lowest concentration to the highest concentration. Before adding each of the components, it was verified if its appearance was homogeneous and lacked turbidity, otherwise a pre-treatment was carried out. The empty containers were weighed, and the respective biofuel was added first, followed by Jet Fuel, recording each of the measured masses, and verifying these values with a re-weighing of the entire system. The addition of each component to the mixture was done in such a way that the entry of air was avoided as much as possible. Once the mixture was obtained, magnetic stirring was carried out using a Fisher Scientific 00781 stirrer at 125 rpm for 20 minutes or more in cases in which not a single liquid phase was observed at the end. Finally, the freezing point was evaluated for each of the 12 samples following the standards established by ASTM D-2386. This test determines the temperature below which solid hydrocarbon crystals can form in aviation fuels.

2.2 Model

Reviewing the models for determining the solidification curves of liquid mixtures, it was decided to start from the phase equilibrium theory to predict both the freezing and melting curves for the solid-liquid equilibrium. Therefore, in equilibrium, the equality of the chemical potentials of any species must be fulfilled in both phases: liquid (L) and solid (S). This leads to the fugacity of that species in the liquid phase of the mixture, $\hat{f}_{i,L}$, being equal to the fugacity of that species in the solid phase of the mixture, $\hat{f}_{i,S}$, such as shown in Equation 1 (Quiroga, 2004).

$$. \ \hat{f}_{i,L} = \hat{f}_{i,S} \tag{1}$$

The development of the previous equation leads to Equation 2 (Smith et al., 2007):

$$x_i \gamma_{i,L} f_{i,L} = z_i \gamma_{i,S} f_{i,S} \tag{2}$$

where x_i and z_i are the mole fractions of component i in the liquid and solid phase respectively during equilibrium. While γ corresponds to the activity coefficient and f to the fugacity of the pure species.
If the relationship between the fugacities of the pure component i in the solid phase and the liquid phase is called ψ_i, then Equation 3 is obtained:

$$x_i \gamma_{i,L} = z_i \gamma_{i,S} \psi_i \tag{3}$$

If the variations between the heat capacities of the liquid and solid phases for each component are neglected (Equation 4):

$$\psi_i = \frac{f_{i,S}}{f_{i,L}} = \exp \frac{\Delta h_{m_i}}{R} \left(\frac{1}{T_{m_i}} - \frac{1}{T} \right) \tag{4}$$

where Δh_{m_i} is the latent heat of fusion of species i, R is the universal gas constant, T_{m_i} is the melting (or freezing) temperature of pure component i, while T is the transition temperature from the liquid phase to the solid phase of the mixture, with which the freezing and melting curves are determined.
Considering a binary mixture of components 1 and 2, where both phases are ideal for all temperatures and compositions, it is found that $\gamma_{i,L} = 1$ and $\gamma_{i,S} = 1$, Equation 3 becomes the system of equations of Expression 5:

$$\begin{cases} x_1 = z_1 \, \psi_1 \\ x_2 = z_2 \, \psi_2 \end{cases} \tag{5}$$

Since the $\sum x_i = 1$ y $\sum z_i = 1$, Expression 5 reduces to Expression 6, which is the model that will be used to predict both curves.

$$\begin{cases} x_1 = \dfrac{\psi_1(1-\psi_2)}{\psi_1-\psi_2} \\ z_1 = \dfrac{1-\psi_2}{\psi_1-\psi_2} \end{cases} \tag{6}$$

Where:

$$\psi_1 = \exp\frac{\Delta h_{m_1}}{R}\left(\frac{1}{T_{m_1}}-\frac{1}{T}\right) \quad \wedge \quad \psi_2 = \exp\frac{\Delta h_{m_2}}{R}\left(\frac{1}{T_{m_2}}-\frac{1}{T}\right)$$

Finally, search for data from the substances analysed to develop the chosen model. Suppose any of the species is a mixture. In that case, its thermophysical properties (such as molar mass and density, as well as temperature and heat of melting) correspond to the component in the highest proportion. Then, Jet Fuel A1 is 2,4-dimethyl undecane (Alirio Benavidez, 2020), for FAME biodiesel of palm oil is methyl palmitate (Lam & Lee, 2011) and FAME biodiesel of palm kernel oil is methyl laurate (Pantzaris & Jaaffarahmad, 2002). While even with ethanol because it is a pure substance. Table 1 shows the respective properties of these 4 substances. Both the density and molar mass values allowed converting the volume proportions of the mixtures to mole fractions.

Table 1: Properties of Species.

Property	Jet A-1 (2,4 dimethyl-undecane)	Palm Oil FAME (methyl palmitate)	Palm Kernel Oil FAME (methyl laurate)	Ethanol
Molar mass (kg/mol)	0.1844	0.2705	0.2143	0.0461
Density (kg/m^3)	800.0000	852.0000	870.0000	789.0000
Molar Volume, (m^3/mol)	0.0002	0.0003	0.0002	0.00006
Melting Temperature, T_m (K)	205.7700	304.0000	278.4500	159.0200
Melting Enthalpy, ΔH_m (kJ/mol)	22.3800	60.0400	43.1500	3.1700
Critical Pressure, P_c, (bar)	16.6597	12.7187	17.0753	61.4800
Critical Temperature, T_c, (K)	662.4413	765.6000	712.1500	513.9000
Acentric Factor, ω	0.5660	0.8644	0.7623	0.6450

3. Results and Discussion

Below, for each of the three systems (ethanol-Jet Fuel A1, palm oil biodiesel-Jet Fuel A1, and palm kernel oil biodiesel-Jet Fuel A1), the results obtained in the experimental determination are presented which are reported by Mayorga et al (2021). The curves obtained for the liquid-solid phase change for each type of mixture are also exposed, as well as the values predicted by the model. Finally, for each of the different proportions of mixtures, the relative error of the freezing temperature emanating from the model concerning that measured experimentally was calculated, for which it is essential to consider that the temperatures must be on an absolute scale.

3.1 Mixtures with Ethanol

Figure 1 shows that the solid-liquid equilibrium curves predicted by the model are very distant and below the experimental values, which indicates that the ideality of the mixture is not fulfilled in the model because ethanol is a molecule with polarity, while those of Jet Fuel A1 kerosene are nonpolar. And also the shapes and sizes of the molecules are very different, so the activity coefficients must be calculated with some thermodynamic equation. This generates that the experimental errors of the model are around 20% as evidenced in Table 2.

Table 2: Comparison between both determinations for the freezing temperature of the Jet Fuel A1-ethanol mixtures.

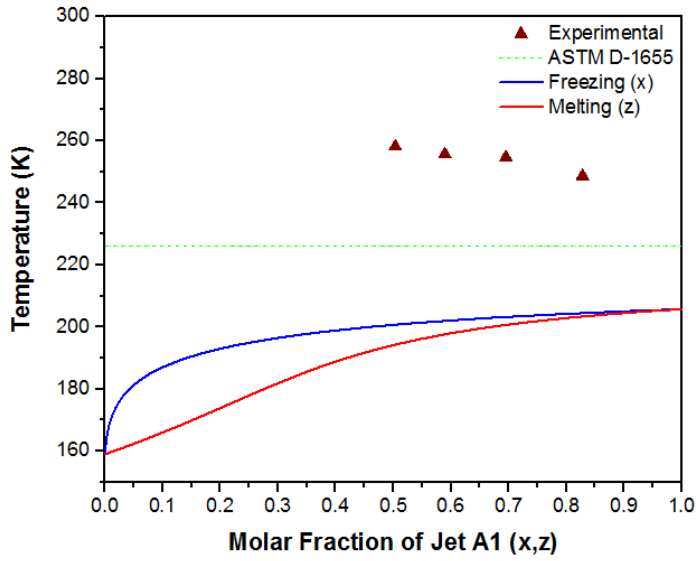| % Volume of Mixture		% Molar of Mixture		Freezing Temperature (K)		Error (%)
Ethanol	Jet A1	Ethanol	Jet A1	Experimental	Model	
5	95	17.20	82.80	248.65	204.50	17.76
10	90	30.48	69.52	254.65	203.00	20.28
15	85	41.05	58.95	255.65	202.00	20.99
20	80	49.66	50.34	258.15	200.50	22.33

Figure 1: Experimental and predictive determination for Jet Fuel A1-ethanol mixtures.

3.2 Palm Oil FAME (PO FAME)

Unlike the previous system with ethanol, Figure 2 shows a greater convergence between the values produced by the model and those measured experimentally, and in Table 3, the error is verified with the calculation, which is an absolute value of a quantity around 2%, it seems that the higher the concentration of biofuel, the model values tend to be below the measurements. Despite containing oxygen, methyl palmitate, being practically nonpolar for the length of the carbon chain, tends to be more affinity to hydrocarbons than ethanol, so the ideal mixture is correct.

Table 3: Comparison between both determinations for the freezing temperature of Jet Fuel A1-PO FAME mixtures.

% Volume of Mixture		% Molar of Mixture		Freezing Temperature (K)		Error (%)
PO FAME	Jet A1	PO FAME	Jet A1	Experimental	Model	
5	95	3.68	96.32	254.15	259.69	2.18
10	90	7.46	92.54	262.65	267.98	2.03
15	85	11.36	88.64	279.65	273.18	-2.31
20	80	15.36	84.64	282.65	277.07	-1.97
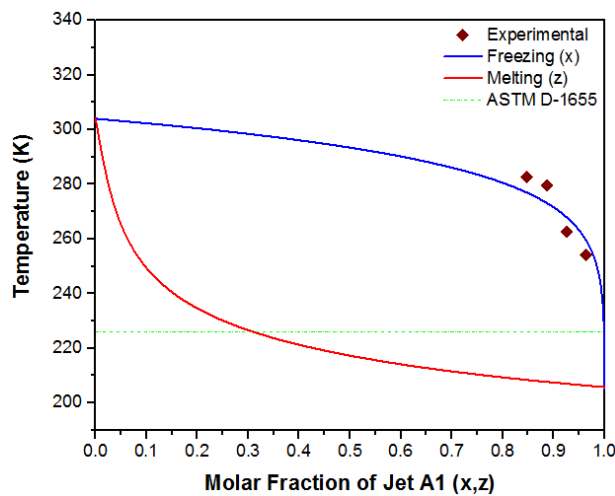
3.3 Palm Kernel Oil FAME (PKO FAME)

The behaviour of the PKO FAME with Jet Fuel is similar to the FAME biodiesel blend of palm oil as discussed in the previous item, with the difference that at a higher concentration of biodiesel, the model seems to tend to fit better than the experimental data as observed both in the absolute errors of Table 4, and in Figure 3. The mean error is also around 2%. This may be because methyl laurate as a model compound of PKO FAME is more predominant and with less competition than methyl palmitate (with 45%) in PO FAME, since the latter competes with methyl palmitate (40 %). Of all samples, the most diluted mixture in PKO FAME (5% by volume) was the closest to meeting the ASTM standard.

Table 4: Comparison between determinations for the freezing temperature of Jet A1-PKO FAME mixtures.

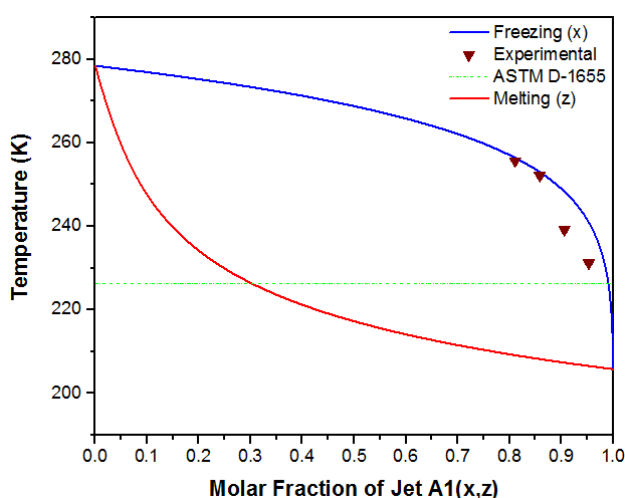| % Volume of Mixture		% Molar of Mixture		Freezing Temperature (K)		Error (%)
PKO FAME	Jet A1	PKO FAME	Jet A1	Experimental	Model	
5	95	4.69	95.31	231.15	241.00	4.26
10	90	9.41	90.59	239.15	248.00	3.70
15	85	14.17	85.83	252.15	253.00	0.34
20	80	18.95	81.05	255.65	256.00	0.14

Figure 3: Experimental and predictive determination for Jet Fuel A1-PKO FAME mixtures.

4. Conclusions

For the blends with ethanol, the error was about 20%, while for both biodiesel from palm oil (methyl palmitate) and palm kernel oil (methyl laurate) is barely 2%. Almost in all cases, it is observed that by increasing the amount of biofuel in the mixture, the model tends to reduce the error in the prediction. Methyl laurate, being a shorter ester molecule, tends to have a lower freezing point compared to palmitate, and closer to Jet Fuel A1. At the same time, the freezing point of ethanol is too low. There are also effects due to the differences in polarity that lead to solutions in both the solid and liquid phases not being ideal as it was considered. Although none of the 12 samples met the ASTM standard, biodiesel blends with A1 jet fuel in concentrations less than 5% by volume could have values less than or equal to -47 °C; according to the model this could be around 1% (mol) of the biofuel. Finally, by lifting non-ideality constraints, contemplating immiscibility and even adding more components to the calculus (not just the more significant proportion) the model can be adjusted to have a lower prediction error.

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