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Study on Physicochemical Properties of Tailor-Made Green Jet Fuel Blend from Waste Cooking Oil

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The International Air Transport Association (IATA) intended to reduce the greenhouse gases (GHG) emissions from the aviation industry by 50 % in 2050 compared to the year 2005. Waste cooking oil (WCO) contains accumulated free fatty acids that make it a technically viable feedstock for conversion to biofuel. Its potential application in jet fuel received huge interest in recent years due to its low price and widely available. The use of waste cooking oil could avoid the inter-competition between the oil resources and edible oil-based food crops, reducing reliance on fossil fuels while also lowering harmful emissions, especially carbon dioxide (CO_2). The main objective of this study is to study the physico-chemical properties of the formulation of jet fuel blend with waste cooking oil. The computer-aided approach was utilised to find the optimum jet fuel blends. The reliability of the computational design approach is dependent on the accuracy of the property prediction models. The critical jet fuel target properties are density, kinematic viscosity, heating value flash point and freezing point. The mixture properties can be predicted using Kay's mixing rule and the Arrhenius mixing rule (for kinematic viscosity only) with high accuracy. The flash point and freezing point prediction models suitable for the prediction of jet fuel properties were identified and verified in this study. This study found that model 1 (freezing point) and model 2 (flash point) have the lowest average percentage error (APE), which are 2.10 % and 0.32 %. These models were used to find the optimal blends of jet fuel. Blend 1 (hydrotreated waste cooking oil C – 92 %, jet fuel C – 8 % by volume) was identified as the optimum green jet fuel blend that satisfied all the target properties of jet fuel. The verified models for flash point and freezing point serve as convenient models for solving the green jet fuel blend design problem.

1. Introduction

Aviation accounts for a small but rising share of global CO_2 emissions (2-3 %), with the highest growth in South East Asia (Roda et al., 2015). Under normal business growth, the International Civil Aviation Organization (ICAO) predicts that global CO_2 emissions from aviation will triple by 2050 (Graver et al., 2019). With such a rapid growth rate, the International Air Transport Association (IATA) decided to cut GHG emissions from the aviation industry by half by 2050, using 2005 global emissions as a baseline. In an era of increasingly volatile oil prices and supply instability due to the depletion of fossil fuels, developing an alternative jet fuel for the aviation industry is critical to ensure sustainable development and reduce its carbon footprint.

Several strategies have been developed to contribute to the CO_2 emissions reduction target. One of the promising strategies is producing alternative jet fuel. The first alternative jet fuel was synthetic paraffinic kerosene (SPK-FT), developed using the Fischer-Tropsch process (ElGalad et al., 2018). Other synthetic bio-based hydrocarbons, such as isoparaffin, naphthene, and aromatics that fall within the jet fuel range (C9-C16), are also promising alternative jet fuel. They can be blended up to 50 % with jet fuel. These blends lack aromatic and polar compounds, which are responsible for fuel lubricity and compatibility with existing fuelling systems. Low-aromatic-compound jet fuel also may cause problems in aircraft fuel system seals.

Waste cooking oil (WCO) is the oil residue obtained after the cooking process, which contains accumulated free fatty acids that makes it a technically viable feedstock for conversion to biofuel. Simasatitkul and Arpornwichanop (2019) studied the potential of WCO as green diesel. Recently, its potential application in jet fuel has attracted huge interest in recent years due to its low price and availability. The use of WCO and

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synthesis of bio-kerosene as a blending agent for commercial jet fuel is intriguing, as most of the WCO is wasted or unusable and disposed of in landfill. The use of WCO could avoid the inter-competition between the oil resources and edible oil-based food crops, reducing reliance on fossil fuels while also lowering harmful emissions, especially CO_2. WCO can produce hydrocarbon products within jet fuel's required carbon range and are suitable feedstock for green jet fuel (Zhang et al., 2019).

Since green jet fuels have recently attracted great interest as alternatives for conventional jet fuels, studies on the possible feedstock or assessments of green jet fuels have been conducted widely and extensively. In recent years, it has been reported that waste cooking oil is a suitable feedstock to be blended into jet fuel (El-Araby et al., 2020). To date, few studies are there are few studies focusing on the physicochemical properties of bio-jet fuels blended from waste cooking oil. To design the optimal bio-jet fuel and give the best performance, the composition of the bio-jet fuel is critical. Although the computational approach is a more efficient and cost-effective option to screen out the most promising blend candidates, experimental work is used in most studies on the formulation of biodiesel-jet fuel blends. Only a few studies on the formulation of bio-jet fuel using the computational technique have been reported.

The accuracy of property prediction models is important in the formulation. Most flash point and freezing point prediction models predicted the flash point and freezing point based on composition or pure component property, for example, the Liaw model (Liaw et al., 2011). To use these models, the composition of the compound needs to be identified. Detailed jet fuel composition is hardly reported in the literature, and hydrotreated waste cooking oil (HCO) composition varies. Alternative prediction models are needed to predict the flash point and freezing point based on the blending index. The accuracy of these models is still unidentified. The objective of this study is to identiy a reliable model for property prediction. This model was used to identify the optimum green jet fuel blends.

2. Methodology

The method is divided into two parts, where the first part is property model identification and validation. The second part is for design of the optimal green jet fuel using a computational-aided method by utilizing the best models from part 1.

2.1 Freezing point and flash point prediction models

Model 1 of the freezing point was proposed by Al Mulla and Albahri (2017) as shown in Eqs(1) – (3).

$$I_{fr,i} = 3.23 \times 10^{-6} \times 1.067^{T_{fr,i}} \quad (1)$$

$$I_{fr,mix} = \sum(v_i \, I_{fr,i}) \quad (2)$$

$$T_{fr,mix} = 193.7 + 15.4 \ln(I_{fr,mix}) \quad (3)$$

where $I_{fr,i}$ is the freezing point index for fuel component i, $T_{fr,i}$ is the freezing point of component i in Kelvin (K), $I_{fr,mix}$ is the blending freezing point index, v is the volume fraction of the component, and $T_{fr,mix}$ is the freezing point of the fuel blend in K.

Model 2 was adopted from study by El-Maghraby (2020) represented by Eqs(4) –(5). There are two different equations designed to calculate blending index depending on the value of the freezing point. Eq(4) is to calculate the blending index for the component that has freezing point that smaller
or equal to 0 °C while Eq(5) is for the component that has freezing point higher than 0°C.

$$I_{fr} = 10^{(0.010332 \, T_{fr} + 1.5506)} \quad , \quad T_{fr} \leq 0 \quad (4)$$

$$I_{fr} = 10^{(0.016644 \, T_{fr} + 1.5554)} \quad , \quad T_{fr} > 0 \quad (5)$$

where I_{fr} is the freezing point index, T_{fr} is the freezing point in degree Celsius (°C). Experimental freezing point data of the binary systems decane–dodecane (Amoabeng, 2014), tetradecane–hexadecane (Dao et al., 2010), stearic acid–methyl stearate (Bailey et al., 1972), methylcyclohexane–heptanol (Zhao et al., 2017), HEFA–Jet A-1 (Starck et al., 2016) and deoxygenated palm kernel oil–Jet A-1 (Why et al., 2021) in a range of 342 – 147 K were used to validate the suitability of Model 1 and Model 2 for the green jet fuel blend formulation. These mixtures were selected because of the similar mixture type as the intended product, which is the mixture of jet fuel and waste cooking oil.

The prediction Model 1 of the flash point proposed by Wickey and Chittenden (1963) shown in Eq(6), Model 2, Eq(7) was developed by Riazi et al. (2005), and Model 3 Eq(8) was proposed by Gary and Handwerk (2001).

$$\log(I_{FP}) = -6.1188 + \frac{2414}{T_{FP} + 503.71} \quad (6)$$

$$I_{FP} = (T_{FP})^{1/-0.06} \quad (7)$$

$$I_{FP} = 51708 \exp\left[\frac{(\ln(T_{FP}) - 2.6287)^2}{-0.91725}\right] \quad (8)$$

where I_{FP} and T_{FP} are the flash point index and the flash point of fuel component in Kelvin (K). A set of experimental values of the binary systems docane–nonane (Li et al., 2014), heptane–o-xylene (Hristova, 2013), pentanol–toluene (Pan et al., 2015), 2-methyl-2-pentanone–butanol (Hristova and Damgaliev, 2013), methyl palmitate–methyl stearate (Dias et al., 2019), HEFA–Jet A-1 (Starck et al., 2016) and deoxygenated palm kernel oil–Jet A-1 (Why et al., 2021) in a range of 455 – 269 K were used to validate the selected models.

2.2 Green jet fuel blends design

A computational approach using Excel solver is used to design bio-jet fuel blends which fulfilled the requirements and achieve optimal performance. Conventional jet fuel is used as the main ingredient and blended with HCO to minimise the usage of fossil-based fuel. The properties of the conventional Jet A-1 fuel was obtained from Starck et al. (2016) and HCO was collected from Why et al. (2021). The target attributes for a tailor-made green jet fuel blend are defined, which covered environmental impact, product performance, and safety. These attributes are translated into target properties and target values as shows in Table 1. The target values for these properties were set based on the ASTM D7566 standard for conventional aviation fuels.

Table 1: Properties and their target values of tailor-made jet fuel

Target Property, ξ	Lower bound (LB) Value	Upper bound (UB) Value
Heating Value, MJ/kg	42.8	-
Density, 15 °C, kg/m^3	775	840
Kinematic Viscosity, 40 °C, cSt	-	8
Flash Point, °C	38	-
Freezing Point, °C	-	−47

The tailor-made jet fuel blending problem is formulated as an optimisation problem with the ultimate goal of generating a tailor-made green jet fuel blend that has the minimum fossil-based jet fuel while satisfying specified constraints on fuel properties. The problem is formulated as an optimisation problem, as shown by Eqs(9)-(10). The problem was solved using an Excel solver.

$$f_{obj} = \min x_{conv} \quad (9)$$

$$\textit{Subject to:} \quad LB_j \leq \sum_{i=1}^{NC} x_i \xi_{i,j} \leq UB_j \qquad \forall j \quad (10)$$

where x_{conv} is the composition of the conventional jet fuel, x is the composition of the blend, LB and UB are the lower and upper bound target values, and ξ is the target property. Subscripts i and j represent component i and property j.

3. Results and discussion

3.1 Freezing point prediction model validation

Two freezing point prediction models proposed by AlMulla and Albahri (2017) and implemented by El-Maghraby (2020) were compared. Figure 1 shows the correlation between the predicted and experimental freezing points using models 1 and 2. The plots indicate a reasonable agreement between the predicted and experimental freezing point values.

The prediction accuracy of the freezing point prediction models is tabulated in Table 2. The average absolute error (AAE) between the theoretical and experimental values of the test sets was within ±15 K. It is worth mentioning that the high difference between the theoretical and experimental values for the deoxygenated palm kernel oil–Jet A-1 system, which is 12.74 K and 9.12 K for model 1 and 2. It is due to the interaction of the mixture, isomerisation of n-paraffins to isoparaffins occurred at room temperature during the blending of deoxygenated palm kernel oil with Jet A-1 fuel (Why et al., 2021). By comparing the prediction performance of both models, the prediction accuracy of Model 1 (2.1 % APE) is better than that of Model 2 (2.5 %).

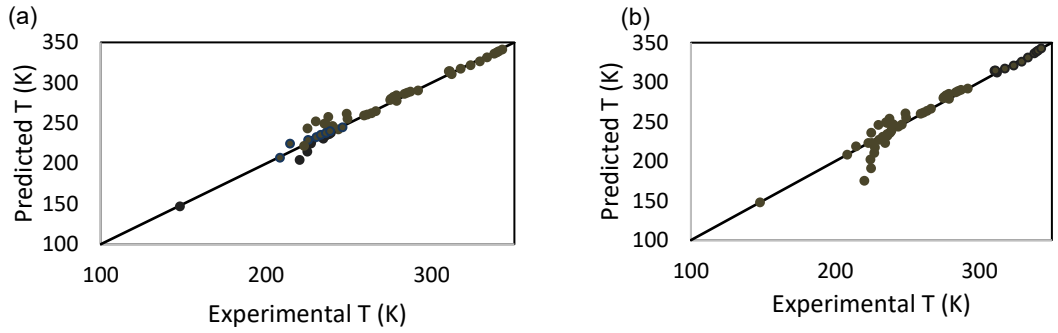

Figure 1: Predicted and experimental freezing point using (a) Model 1 and (b) Model 2

Table 2: Absolute average error (AAE) and average percentage error (APE) of the freezing point model

Mixture	Model 1 AAE	Model 1 APE(%)	Model 2 AAE	Model 2 APE(%)
Decane + dodecane	5.32	2.22	4.94	2.07
Tetradecane + hexadecane	3.28	1.17	3.77	1.35
Stearic acid + methyl stearate	1.94	0.60	1.80	0.56
Methylcyclohexane + heptanol	3.93	1.76	13.86	6.15
HEFA + Jet A-1	3.07	1.37	1.85	0.82
Deoxygenated palm kernel oil + Jet A-1	12.74	5.44	9.12	3.88

3.2 Flash point prediction model validation

Figure 2 shows the correlation between the predicted and experimental freezing points using the three models. The plots indicate a good agreement between the predicted and experimental flash point values. The resulting AAE and APE of the test sets are shown in Table 3. A satisfactory accuracy was observed. The results for all models show the AAE values for test sets are within the experimental error of flash point determination, which is around ±10 K (Botros and Atkenson, 1990). The results showed that the model predictions for all the test sets were accurate, with percentage errors lower than 5 %. It indicates that these three models are reliable to predict the flash point of the mixtures, including the fuel blends. By comparing the prediction performance of the three models from Table 2, the results of Model 2 are very close to or even a little better than those of the other two models for the test sets for models 1 and 3.

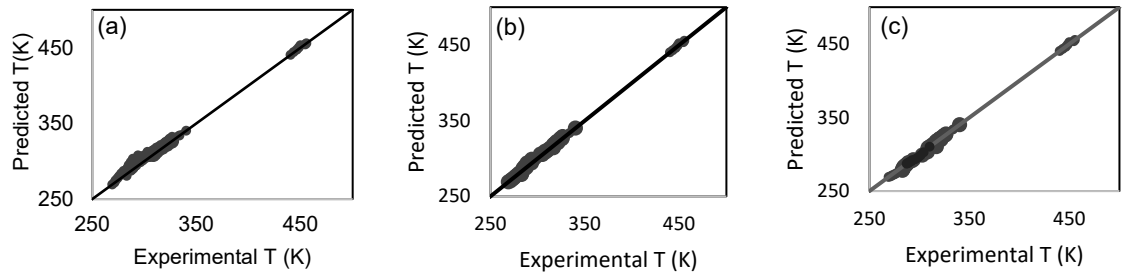

Figure 2: Correlation between predicted and experimental flash point using (a) Model 1 (b) Model 2 (c) Model 3

Table 3: Absolute average error (AAE) and average percentage error (APE) of the flash point models

Flash Point Model	Model 1		Model 2		Model 3	
Mixture	AAE	APE (%)	AAE	APE(%)	AAE	APE(%)
Decane + nonane	0.92	0.29	0.36	0.11	0.67	0.21
Heptane + o-xylene	4.14	1.47	0.42	0.15	2.67	0.94
Pentanol + toluene	7.42	2.55	2.86	0.98	3.14	1.06
4-methyl-2-pentanone + butanol	1.89	0.64	0.39	0.13	1.28	0.43
Methyl palmitate + methyl stearate	1.09	0.24	0.61	0.14	0.61	0.14
HEFA + Jet A-1	3.49	1.08	1.31	0.41	0.48	0.15
Deoxygenated palm kernel oil + Jet A1	2.25	0.70	1.14	0.36	0.71	0.22

3.3 Formulation results of jet fuel-hydrotreated waste cooking oil blends

There was a total of twelve jet fuel – hydrotreated waste cooking oil blends obtained. The maximum vol% of the HCO in the four Jet A-1 are as in Table 4. The results have shown that the HCO could be blended in a significant amount in conventional jet A-1 fuel. HCO A can be incorporated at up to 66 % before failing to achieve the minimum total aromatics content. HCO B found it unsuitable for blending with jet fuel due to its high freezing point. It can only be blended up to 7 %. HCO C was found can be incorporated at up to 92 % volume before failing Jet A-1 density. The incorporation ratio is dependent of the conventional jet fuel quality. The current ASTM specification limits the incorporation rate of hydroprocessed ester and fatty acids to a maximum of 50 % volume. However, there has no physics-based limit that limits the incorporation rate of biojet fuel. The ASTM specification limits might be due to the limited amount of biojet fuel generated. These results have shown the potential to enhance the incorporation of hydro-processed biojet fuel in conventional jet fuel.

Table 4: Maximum blend of HCO-Jet A-1 combinations without composition limitation

HCO	Jet A-1	Limit (vol%)	Limiting Property
HCO A	JF A	65.17	Aromatic Content
	JF B	56.64	Aromatic Content
	JF C	66.30	Aromatic Content
	JF D	65.36	Aromatic Content
HCO B	JF A	2.46	Freezing Point
	JF B	2.14	Freezing Point
	JF C	6.57	Freezing Point
	JF D	3.72	Freezing Point
HCO C	JF A	88.92	Density
	JF B	87.89	Density
	JF C	92.18	Density
	JF D	90.63	Density

These optimum blends are ranked according to the blending ratio. All the resulting blends have met the ASTM specification and their properties are comparable to the jet fuel-HEFA blends studied by Stark et al. (2016). It indicates that HCO oil is a promising source for biojet fuel production to replace vegetable oil, solving the food-energy crisis and waste problem. Blend 1 was selected as the optimum green jet fuel blend owing to its high hydrotreated waste cooking oil blending ratio. Table 5 presents the properties of the HCO–Jet A-1 blends.

Table 5: Formulated HCO–Jet A-1 blends and the estimated properties

Blend	Formulation	ρ (kg/m^3)	AC (vol%)	HV (MJ/kg)	T_{FP} (°C)	T_{fr} (°C)	η (cSt)
1	0.92 HCO C + 0.08 JF C	775.00	8.22	43.69	43.42	-53.44	3.56
2	0.91 HCO C + 0.09 JF D	775.00	8.37	43.76	44.08	-52.90	3.60
3	0.89 HCO C + 0.11 JF A	775.00	8.57	43.69	44.34	-52.59	3.57
4	0.88 HCO C + 0.12 JF B	775.00	8.28	43.68	43.11	-52.49	3.57
5	0.66 HCO A + 0.34 JF C	780.49	8.00	43.68	42.17	-58.34	3.93
6	0.65 HCO A + 0.35 JF D	778.19	8.00	43.98	44.64	-55.20	4.04
7	0.65 HCO A + 0.35 JF A	776.06	8.00	43.77	45.13	-54.01	3.90
8	0.57 HCO A + 0.43 JF B	778.72	8.00	43.69	21.33	-53.31	3.90
9	0.07 HCO B + 0.93 JF C	819.02	18.91	43.06	43.57	-47.00	4.16
10	0.04 HCO B + 0.96 JF D	811.89	18.99	43.91	51.55	-47.00	4.52
11	0.02 HCO B + 0.98 JF A	805.92	19.13	43.32	53.35	-47.00	4.09
12	0.02 HCO B + 0.98 JF B	803.03	15.77	43.26	40.85	-47.00	4.03

4. Conclusions

In summary, two freezing point property prediction models and three flash point property prediction models were validated and compared. Model 1 (freezing point) and Model 2 (flash point) were found to have the lowest average percentage error (APE), which are 2.10 % and 0.32 %. The designed green jet fuel blends strictly met the ASTM standard. It has been shown that these HEFA can be blended in significant volumes in a conventional Jet A-1. The upper limits in terms of incorporation are the aromatic content of the final blend for the introduction of HCO A, the freezing point for HCO B and the density for HCO C. Among the tailor-made green jet fuel blends generated, Blend 1 (hydrotreated waste cooking oil C – 92 vol%, jet fuel C – 8 vol%) was identified to be the

optimum green jet fuel blend owning to its high hydrotreated waste cooking oil blending ratio, which in turn results in lower greenhouse gas emission.

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