A Hybrid Thermodynamic–Machine Learning Approach for Flash Point Prediction of Binary Organic Mixtures

Un enfoque híbrido termodinámico-aprendizaje automático para la predicción del punto de inflamación de mezclas orgánicas binarias

Uma abordagem híbrida de termodinâmica e aprendizado de máquina para a previsão do ponto de fulgor de misturas orgânicas binárias

Nadia Khan [1], Ahmed Saleem [2], Aisha Jilani [3], Asad A. Zaidi [4] (*)

Recibido: 04/02/2026 Aceptado: 31/03/2026

Summary. - Flash point is a critical safety parameter indicating the lowest temperature at which a flammable liquid mixture can ignite. Accurate flash point estimation is essential for hazard prevention in chemical processing and fuel handling, yet experimental determination is time-consuming, costly, and hazardous. This study presents a combined thermodynamic and machine learning methodology to predict flash points of binary organic mixtures. A Liaw–UNIFAC thermodynamic model was used to generate vapor pressure and activity coefficient inputs, which were then used to train an Artificial Neural Network (ANN) for flash point prediction. The ANN model, configured with four hidden layers (10-20-10-5 neurons), captures complex non-linear relationships between mixture composition, molecular properties, and flash point. Model evaluation against literature data for eight diverse binary mixtures (including alcohols, alkanes, aromatics, and ketones) demonstrates high accuracy: the ANN's flash point predictions show mean squared errors (MSE) below 0.1 and R2 above 0.99 in most cases, closely matching both experimental results and the Liaw–UNIFAC model. The ANN approach offers comparable reliability to the mechanistic Liaw model while significantly improving computational efficiency and adaptability. These findings highlight the potential of hybrid thermodynamic ANN modeling to enhance process safety by enabling rapid, accurate flash point estimation for complex mixtures without exhaustive physical testing.

Keywords: *Flash point; Multicomponent mixtures; Liaw–UNIFAC model; Artificial neural network; Process safety; Non-ideality.*

(*) Corresponding author.

[1] PhD. Polymer & Petrochemical Engineering Department, NED University of Engineering & Technology (Pakistan), nadiakhan@neduet.edu.pk, ORCID iD: https://orcid.org/0009-0009-9029-0091

[2] Master of Engineering. Polymer & Petrochemical Engineering Department, NED University of Engineering & Technology (Pakistan), ahmedsaleem@neduet.edu.pk, ORCID iD: https://orcid.org/0009-0004-4095-7074

[3] Assistant Professor, Polymer & Petrochemical Engineering Department, NED University of Engineering & Technology (Pakistan), aishajilani@neduet.edu.pk, ORCID iD: https://orcid.org/0009-0009-5904-6680

[4] Professor, Department of Mechanical Engineering, Faculty of Engineering, Islamic University of Madinah (Saudi Arabia), engr.sami@neduet.edu.pk, ORCID iD: https://orcid.org/0000-0001-5457-5684

Memoria Investigaciones en Ingeniería, núm. 30 (2026). pp. 189-210
https://doi.org/10.36561/ING.30.13
ISSN 2301-1092 • ISSN (en línea) 2301-1106 – Universidad de Montevideo, Uruguay

Resumen. - *El punto de inflamación es un parámetro de seguridad crítico que indica la temperatura más baja a la que una mezcla líquida inflamable puede encenderse. La estimación precisa del punto de inflamación es esencial para la prevención de riesgos en el procesamiento químico y el manejo de combustibles; sin embargo, la determinación experimental es laboriosa, costosa y peligrosa. Este estudio presenta una metodología combinada de termodinámica y aprendizaje automático para predecir los puntos de inflamación de mezclas orgánicas binarias. Se utilizó un modelo termodinámico Liaw-UNIFAC para generar entradas de presión de vapor y coeficiente de actividad, que luego se utilizaron para entrenar una red neuronal artificial (RNA) para la predicción del punto de inflamación. El modelo de RNA, configurado con cuatro capas ocultas (10-20-10-5 neuronas), captura relaciones no lineales complejas entre la composición de la mezcla, las propiedades moleculares y el punto de inflamación. La evaluación del modelo comparándolo con datos de la literatura para ocho mezclas binarias diversas (que incluyen alcoholes, alcanos, aromáticos y cetonas) demuestra una alta precisión: las predicciones del punto de inflamación de la red neuronal artificial (RNA) muestran errores cuadráticos medios (ECM) inferiores a 0,1 y un coeficiente de determinación (R^2) superior a 0,99 en la mayoría de los casos, coincidiendo estrechamente con los resultados experimentales y el modelo Liaw-UNIFAC. El enfoque de la RNA ofrece una fiabilidad comparable al modelo mecanicista de Liaw, a la vez que mejora significativamente la eficiencia computacional y la adaptabilidad. Estos hallazgos resaltan el potencial del modelado termodinámico híbrido con RNA para mejorar la seguridad de los procesos, al permitir una estimación rápida y precisa del punto de inflamación para mezclas complejas sin necesidad de ensayos físicos exhaustivos.*

Palabras clave: *Punto de inflamación; Mezclas multicomponentes; Modelo Liaw-UNIFAC; Red neuronal artificial; Seguridad de procesos; No idealidad.*

Resumo. - *O ponto de fulgor é um parâmetro crítico de segurança que indica a temperatura mais baixa na qual uma mistura líquida inflamável pode entrar em combustão. A estimativa precisa do ponto de fulgor é essencial para a prevenção de riscos no processamento químico e no manuseio de combustíveis; no entanto, a determinação experimental é demorada, dispendiosa e perigosa. Este estudo apresenta uma metodologia combinada de termodinâmica e aprendizado de máquina para prever o ponto de fulgor de misturas orgânicas binárias. Um modelo termodinâmico de Liaw-UNIFAC foi utilizado para gerar dados de pressão de vapor e coeficiente de atividade, que foram então usados para treinar uma Rede Neural Artificial (RNA) para a previsão do ponto de fulgor. O modelo de RNA, configurado com quatro camadas ocultas (10-20-10-5 neurônios), captura relações não lineares complexas entre a composição da mistura, as propriedades moleculares e o ponto de fulgor. A avaliação do modelo em relação aos dados da literatura para oito misturas binárias diversas (incluindo álcoois, alcanos, aromáticos e cetonas) demonstra alta precisão: as previsões do ponto de fulgor da RNA apresentam erros quadráticos médios (EQM) abaixo de 0,1 e R^2 acima de 0,99 na maioria dos casos, correspondendo de perto tanto aos resultados experimentais quanto ao modelo Liaw-UNIFAC. A abordagem da RNA oferece confiabilidade comparável ao modelo mecanístico de Liaw, ao mesmo tempo que melhora significativamente a eficiência computacional e a adaptabilidade. Essas descobertas destacam o potencial da modelagem termodinâmica híbrida com RNA para aprimorar a segurança do processo, permitindo a estimativa rápida e precisa do ponto de fulgor para misturas complexas sem testes físicos exaustivos.*

Palavras-chave: *Ponto de fulgor; Misturas multicomponentes; Modelo Liaw-UNIFAC; Rede neural artificial; Segurança de processos; Não idealidade.*

1. Introduction. - Flash point, defined as the minimum temperature at which a volatile liquid produces sufficient vapor to ignite in air, is a fundamental indicator of fire and explosion hazard. In industrial practice, knowledge of a material's flash point underpins safe handling, storage, and transport guidelines[1, 2].A lower flash point signifies higher flammability; thus even modest changes in mixture composition can markedly affect safety classification [3]. For example, blending a small fraction of a low-flash solvent into a fuel can dramatically reduce the overall flash point, raising the risk of ignition. As new chemicals and fuel blends are introduced in the petrochemical, pharmaceutical, and agrochemical sectors, there is an increasing need for accurate flash point data to ensure process safety and regulatory compliance[4-6].

Traditional flash point determination relies on standardized experimental methods (Pensky-Martens closed-cup or Tag open-cup tests per ASTM protocols) which, while accurate, have significant limitations. Experimental testing of every possible mixture is labor-intensive, time-consuming, and often impractical when dealing with hazardous, toxic, or radioactive substances. Moreover, experiments become prohibitively expensive and slow when exploring large compositional design spaces or optimizing fuel blends [3, 7, 8]. These drawbacks motivate the development of predictive models to estimate mixture flash points rapidly and safely.

Several thermodynamic models have been proposed to predict mixture flash points by leveraging underlying vapor–liquid equilibrium relationships. One widely used approach is the Liaw model, which is grounded in Raoult's law and assumes flash point occurs when the mixture's total vapor pressure equals the lower flammability limit (LFL) partial pressure of fuel vapor in air [9, 10].The Liaw model requires vapor pressure of each component (often obtained via Antoine equations) and activity coefficients to account for non-ideal liquid-phase interactions. Group-contribution methods like UNIversal Functional Activity Coefficients (UNIFAC) UNIversal Functional Activity Coefficients are commonly coupled with the Liaw model to estimate activity coefficients without extensive binary interaction data [2, 11]. The combined Liaw–UNIFAC flash point model has shown good accuracy for a variety of mixtures and has become a reference method in flash point prediction. However, the Liaw model is iterative and requires calibration of certain parameters (e.g. fuel average structures, LFL values) for each mixture system. Its accuracy can degrade for systems with strong non-idealities (e.g. associating or partially miscible mixtures) or when extrapolating beyond conditions used in its parameterization. Extensions employing NRTL, Wilson, UNIQUAC, or COSMO-RS activity coefficient models have been used to improve predictions for complex mixtures, but these still rely on detailed physicochemical data that may not be readily available [8, 12, 13].

An alternative paradigm is quantitative structure property relationship (QSPR) modeling, wherein flash point is correlated to molecular descriptors. Early QSPR efforts for flash point focused on pure compounds and achieved moderate success using descriptors such as boiling point or functional group counts. For mixtures, QSPR is more challenging due to the need to encode interactions between components. More recently, machine learning approaches have gained traction. Notably, artificial neural networks (ANNs) have been applied to predict flash points by learning from experimental data. ANNs can capture complex non-linear relationships and can improve as more data are added [14, 15]. Aljaman et al.[16] developed a neural network model incorporating functional group counts and molecular parameters to predict flash points of oxygenated fuel mixtures, achieving a regression coefficient R2 approx 0.98. Other studies have similarly reported that ANN models perform on par with or even better than mechanistic models for flash point prediction of pure substances and simple mixtures [17]. A key advantage of ANNs is their flexibility: once trained on a sufficiently broad dataset, an ANN can rapidly predict flash points for new mixtures without additional physical input, aside from readily computed descriptors. This makes the approach attractive for screening large candidate sets (e.g. in solvent substitution or fuel formulation) and for complex mixtures where parameterizing an activity coefficient model is cumbersome [18].

Purely mechanistic models (like Liaw–UNIFAC) may struggle with mixtures exhibiting atypical phase behavior, such as partial miscibility or azeotrope-like extremes, due to underlying model assumptions. QSPR and ANN models, on the other hand, are data-driven and can be limited by the scope and quality of training data – they may not extrapolate well beyond the range of compositions or chemistries seen in their training set. There is thus a gap in leveraging both approaches: by integrating fundamental thermodynamic calculations (to enforce physical consistency) with machine learning (to capture residual nonlinear trends), one can potentially achieve more robust predictions across a wider domain of mixtures.

This work addresses the aforementioned gap by proposing a hybrid modeling approach. We use the Liaw–UNIFAC model to generate intermediate parameters (vapor pressures and activity coefficients) that inform an ANN, effectively blending domain knowledge with data-driven learning. The novelty lies in using the ANN to refine and extend the flash point predictions beyond the immediate capabilities of the Liaw model – for example, handling diverse functional groups and mixture types without re-estimating interaction parameters for each new system. The contribution of this study is twofold: (1) demonstrating that an ANN can be trained to emulate and augment a thermodynamic flash point model with high fidelity, and (2) providing insight into flash point behavior across various mixture classes (alcohol–alcohol, alcohol–hydrocarbon, hydrocarbon–aromatic, hydrocarbon–ketone) through comparative analysis of model predictions and experimental data. By significantly reducing the need for exhaustive experimental flash point measurements, this approach can facilitate safer and faster evaluation of mixture flammability in process design and safety engineering.

2 Methodology. –

2.1 Dataset and Input Variables. - A comprehensive dataset of binary mixture flash points was compiled from literature sources. Based on component functionality and intermolecular interactions, the studied mixtures were grouped into alcohol–alcohol, alcohol–alkane, alkane–aromatic, alcohol mixtures with differing carbon chain lengths, alkane–alcohol, aromatic–alkane, alkane–ketone, and additional alkane–aromatic systems, represented by combinations such as 1-butanol + 2-butanol, 2-butanol + n-octane, n-heptane + o-xylene, ethanol + 2-butanol, octane + 1-butanol, ethylbenzene + n-heptane, n-decane + acetone, and n-heptane + m-xylene.

For each of the eight binary mixtures considered, experimentally measured closed-cup flash point data were collected over a wide composition range, typically spanning the full mole fraction interval (0–1). The number of experimental data points per mixture varied depending on data availability in the literature, generally ranging from 10 to 15 data points per system as shown in Table I. The composition grids were not uniform across all datasets, as measurements were reported at discrete and non-identical compositions by different sources. To preserve data fidelity, all reported experimental data points were retained without interpolation or smoothing. Experimental flash point measurements were obtained using standard closed-cup methods, with typical uncertainties in the range of ±1°C to ±2°C. Where multiple literature sources reported data at similar compositions, consistency checks were performed.

Pure-component vapor pressure behavior was characterized using Antoine equation coefficients (Ai,Bi_and Ci), which enable calculation of saturation vapor pressures over the temperature range relevant to flash point determination. Vapor pressure is a key determinant of mixture flammability, as higher vapor pressures lead to increased fuel vapor concentrations at a given temperature.

Mixture composition was incorporated through the mole fraction of one component (x_1,x_2), allowing the model to capture the continuous variation of flash point across the entire composition domain. Molecular structure effects were represented using UNIFAC functional group counts (e.g., –CH_3,–OH,–CO),which provide a group-contribution description of intermolecular interactions.

Non-ideal solution behavior was quantified via activity coefficients calculated using the UNIFAC method. For each composition, activity coefficients γ_1 ,γ_2 were evaluated at the flash point condition, corresponding to vapor–liquid equilibrium at the lower flammability limit. The logarithmic terms $\ln\gamma_1$ and $\ln\gamma_2$ were included as model inputs to capture deviations from Raoult's law arising from attractive or repulsive molecular interactions.

Additionally, the flash point predicted by the Liaw–UNIFAC model was included as an auxiliary input during ANN training. This hybrid formulation enables the ANN to leverage established thermodynamic relationships while learning systematic residual corrections beyond the mechanistic model. The methodology adopted for this study is shown in Figure I.

All required pure-component properties were obtained from standard data sources, including the NIST Chemistry WebBook and chemical engineering handbooks.

2.1.1 Implementation of the Liaw–UNIFAC Flash Point Model. - Activity coefficients were computed using the UNIFAC method as functions of mixture composition and temperature, accounting for intermolecular interactions and deviations from ideal solution behavior. These coefficients were then incorporated into the Liaw flash point model, which estimates the mixture flash point as the temperature at which the total vapor pressure equals atmospheric pressure under LFL conditions[19, 20].

The Liaw–UNIFAC model was applied to both binary mixtures, serving as a mechanistic reference model and generating intermediate predictions used to guide ANN learning.

2.1.2 Artificial Neural Network Training. - The ANN framework integrated thermodynamic descriptors with data-driven learning to predict closed-cup flash points. The network was trained using mixture composition, Antoine parameters, UNIFAC functional group descriptors, activity coefficients, and Liaw–UNIFAC flash point estimates as inputs, with experimentally measured flash point values as targets where available. Through supervised training, the ANN learned nonlinear relationships between molecular structure, mixture non-ideality, and flammability behavior. The inclusion of physics-based features enabled the network to systematically correct deviations inherent in mechanistic models, resulting in improved predictive accuracy and enhanced generalization across diverse chemical systems [21].

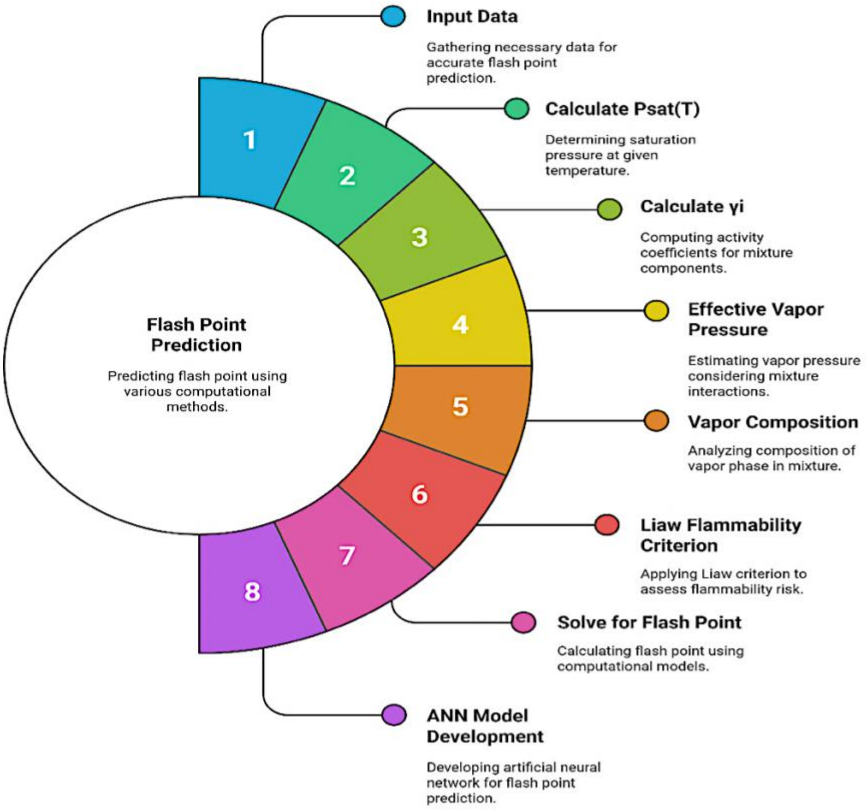


Figure I Process for the binary flash point prediction methodology, integrating Liaw–UNIFAC thermodynamic computations with ANN model training.

2.2 Liaw–UNIFAC Flash Point Model. - The Liaw flash point model provides a thermodynamic framework to compute the flash point of a mixture by satisfying a vapor pressure summation criterion. For a binary mixture, the flash point Tfp is found by solving the equation 1 [22].

$$\sum_{i=1}^{2} y_i\left(T_{fp}\right) = LFL \qquad (1)$$

where yi is the vapor mole fraction of component i in air at equilibrium with the liquid, and LFL is the lower flammability limit (as a mole fraction in air) of the mixture's vapor. Equation (1) represents the general flammability criterion based on the vapor-phase composition at the flash point. The vapor composition can be expressed via Raoult's law with activity coefficients equation 2 [23].

$$y_i = \frac{x_i\, \gamma_i\left(T_{fp}\right) P_i^{sat}\left(T_{fp}\right)}{P_{\mathrm{atm}}} \qquad (2)$$

Here Pisat(T) is the saturation vapor pressure of pure component i (from Antoine equation) using equation 3, γ is the activity coefficient in the liquid mixture (from UNIFAC) and Patm is atmospheric pressure [24]. The UNIFAC method is used to calculate γi at each trial temperature, requiring a breakdown of each molecule into functional groups and utilizing group interaction parameters using equation 4 [25]. UNIFAC accounts for non-ideal mixing effects like hydrogen bonding or polar–nonpolar interactions, which can significantly alter vapor pressures. For example, an alcohol (polar) + alkane (nonpolar) mixture often exhibits activity coefficients γ for the alcohol at high alkane content, indicating positive deviation (the alcohol is less volatile in mixture than ideal, raising the flash point). Activity coefficients were calculated using the original UNIFAC group contribution method. Functional group assignments for each component were performed based on standard UNIFAC group definitions, where molecules were decomposed into constituent functional groups such as $–CH_3$, $–CH_2–$, –OH, and –CO. The required group interaction parameters were taken from established UNIFAC parameter tables reported in the literature. The temperature dependence of activity coefficients was accounted for implicitly through the UNIFAC formulation, where interaction parameters are functions of temperature and composition. All activity coefficient calculations were performed at the estimated flash point temperature during the iterative solution procedure. While the Liaw–UNIFAC model is effective, it requires reliable Antoine constants and UNIFAC group parameters for all components, and the iterative solution can be computationally intensive when embedded in an optimization loop [26]. Moreover, as noted, it may struggle if LFL or certain interaction parameters are not well-characterized.

$$log_{10}\ P^{sat}\left(T\right) = A_i - \frac{B_i}{T + C_i} \qquad (3)$$

$$ln\gamma_i = {\gamma_i}^c + {\gamma_i}^R \qquad (4)$$

Equation (1) essentially finds the temperature at which the total fuel vapor concentration reaches the flammable threshold. The model assumes the fuel vapors behave ideally in the gas phase and that only fuel components (and not air) contribute to the sum (which is valid for low fuel vapor concentrations at flash point).

In practice, for a given x1, the model iterates on Tfp: initially estimating a temperature (e.g. a composition-weighted average of pure component flash points), computing y1 + y2, and adjusting T until y1 + y2 = LFL as shown in equation 5 [22]. By incorporating vapor–liquid equilibrium relationships through saturation vapor pressures and activity coefficients, Eq. (1) can be reformulated into the working expression given in Eq. (5). By incorporating vapor–liquid equilibrium relationships through saturation vapor pressures and activity coefficients, Eq. (1) can be reformulated into the working expression given in Eq. (5). Thus, Eq. (5) represents the practical form of the Liaw model used for flash point calculation under non-ideal conditions.

$$\frac{y_1}{LFL_1} + \frac{y_2}{LFL_2} = 1 \qquad (5)$$

The LFL itself can be estimated or taken from experimental data for similar mixtures; often a value of 0.05 (5% v/v in air) is used as an approximation for hydrocarbon vapors.

Liaw–UNIFAC model is used to generate a flash point estimate and associated γ values for each data point, effectively creating a rich set of features. By doing so, we embed domain knowledge into the ANN, allowing it to learn the discrepancies between this mechanistic prediction and actual observations. In this study, a constant lower flammability limit (LFL) value of 0.05 (5% v/v in air) was adopted as a simplifying assumption. This approximation is commonly used for hydrocarbon systems when detailed mixture-specific flammability data are unavailable.

2.3 ANN Architecture and Training. - An artificial neural network was constructed to map the input variables (composition, Antoine coefficients, group descriptors, UNIFAC etc.) to the output flash point. To identify an optimal ANN configuration, networks with varying numbers of hidden neurons (5–20), different training algorithms and multiple transfer functions were evaluated. Model performance was assessed using RMSE, MAE, and coefficient of determination (R^2) on validation data. It is noted that the current validation approach is based on random datapoint splitting and does not explicitly evaluate model performance on entirely unseen binary systems. After testing various configurations, a feed-forward multilayer perceptron with 20 hidden layers was selected as the best architecture a feed-forward multilayer perceptron with four hidden layers consisting of 10, 20, 10, and 5 neurons in each particular layer, respectively, was selected as the optimal architecture as depicted in Table II and III. This configuration was selected based on a balance between model complexity and generalization performance observed during systematic testing.

Mixture	No. of Data Points	Composition Range (x_1)
1-butanol + 2-butanol	15	0–1
2-butanol + n-*octane*	12	0–1
n-heptane + o-xylene	12	0–1
ethanol + 2-butanol	10	0–1
octane + 1-butanol	10	0–1
ethylbenzene + n-heptane	15	0–1
n-decane + acetone	10	0–1
n-heptane + m-xylene	10	0–1

Table I. Experimental flash point datasets for eight binary mixtures, including number of datapoints, composition range.

No. of Hidden Layer Neurons Number of Neurons in Each Hidden Layer	Mean of Average Standard Deviations in 20 Repeats (Overall)	Mean of Average Standard Deviations in 20 Repeats (Training)	Mean of Average Standard Deviations in 20 Repeats (Validation)	Mean of Average Standard Deviations in 20 Repeats (Test)
10	46.66	0.76154	0.76925	0.80203
20	50	0.7	0.71	0.72
10	46.66	0.76154	0.76925	0.80203
5	42.79	0.82164	0.82722	0.87261

Table II. Performance Metrics for the Mean standard deviation over 20 independent training runs.

The Table III summarizes the performance of different ANN training algorithms and transfer (activation) functions evaluated for flash point prediction. The models were assessed based on prediction efficiency and robustness across repeated training runs.

The column "Nr. Reliable Models" represents the number of training runs that converged to a stable and acceptable solution out of multiple independent initializations, serving as a measure of model robustness and reproducibility. Prediction efficiencies are reported for the overall dataset as well as separately for the training, validation, and test subsets. The results indicate that networks trained using the Levenberg–Marquardt (trainlm) algorithm consistently outperform those trained with gradient descent (traingd) in terms of both accuracy and stability. Among the evaluated transfer functions, logsig achieved the highest prediction efficiency (98.5%) with strong robustness (70 reliable models), while poslin exhibited the greatest robustness (73 reliable models) with slightly lower efficiency (97.8%). The tansig function also showed competitive performance, whereas hardlim and radbas yielded inferior robustness and accuracy, making them unsuitable for continuous flash point prediction. The approximately identical efficiencies observed across validation, and test sets demonstrate excellent generalization strong predictive performance within the studied dataset and indicate the absence of overfitting no significant indication of overfitting within the investigated dataset, attributable to the incorporation of physics-based input features derived from the Liaw–UNIFAC framework.

Training Algorithm	Transfer Function	Nr. Reliable Models	Accuracy % (Overall)	Accuracy % (Training)	Accuracy % (Validation)	Accuracy % (Test)
trainlm	logsig	70	98.5	99.2	98.1	97.8
trainlm	tansig	56	97.2	98.0	96.8	96.5
trainlm	hardlim	0	96.5	97.1	96.0	95.8
trainlm	poslin	73	97.8	98.6	97.2	96.9
trainlm	radbas	25	92.0	93.1	91.5	91.2
traingd	logsig	0	85.0	86.2	84.3	84.0
traingd	tansig	0	84.0	85.0	83.5	83.2
traingd	hardlim	0	83.5	84.6	83.0	82.8
traingd	poslin	0	85.5	86.4	85.0	84.7
traingd	radbas	0	81.0	82.0	80.5	80.2
trainrp	logsig	0	87.0	88.2	86.5	86.0
trainrp	tansig	0	86.0	87.1	85.4	85.0
trainrp	hardlim	0	85.0	86.2	84.6	84.2
trainrp	poslin	12	82.5	83.8	82.0	81.6
trainrp	radbas	0	80.0	81.2	79.5	79.0
trainscg	logsig	23	91.0	92.0	90.5	90.2
trainscg	tansig	13	89.0	90.1	88.5	88.2
trainscg	hardlim	0	88.5	89.6	88.0	87.7
trainscg	poslin	44	90.0	91.2	89.5	89.1
trainscg	radbas	1	88.0	89.0	87.5	87.2
trainbfg	logsig	51	89.5	90.6	89.0	88.6
trainbfg	tansig	3	78.0	79.2	77.5	77.0
trainbfg	hardlim	0	77.5	78.6	77.0	76.5

Table III. Details of reliable ANNs for each combination of transfer function and training algorithm.

During training, the dataset was split 70:15:15 into training, validation, and testing subsets. It is acknowledged that random splitting across individual datapoints may introduce correlation between training, validation, and testing subsets because adjacent compositions within the same binary mixture are not fully independent. The training process employed the Levenberg–Marquardt algorithm combined with the logsig activation function provides the most accurate and reliable ANN configuration for flash point prediction.The ANN weights were initialized randomly (with a fixed random seed for reproducibility) and updated to minimize the mean squared error between predicted and actual flash points. Input features were normalized to zero mean and unit standard deviation, and the flash point outputs were scaled to 0–1 range during training to assist convergence, then rescaled to °C for reporting. It is important to note that the ANN in this study does not simply replicate the Liaw–UNIFAC prediction. Instead, it operates as a correction model that learns residual nonlinear deviations between thermodynamic predictions and experimental flash point values. The inclusion of physically meaningful inputs such as activity coefficients and vapor pressures enables the ANN to capture non-ideal effects beyond the capability of the standalone thermodynamic model.

2.4 Model Evaluation Metrics. - The predictive performance of the developed ANN model was evaluated using the coefficient of determination (R^2) and mean squared error (MSE). The efficiency (%) reported in this study represents the coefficient of determination (R^2) expressed as a percentage. It is noted that the reported efficiency values correspond to overall model performance calculated over the entire dataset rather than being computed separately for training, validation, and testing subsets. This approach was adopted to provide a global assessment of model accuracy.

3. Results and Discussion. - It should be noted that the efficiency values reported in this study represent overall model performance, which may result in approximately identical values across different dataset splits. The results obtained in this study are analyzed by first examining the composition-dependent flash point behavior of the binary mixtures from a thermodynamic standpoint. Subsequently, the predictive performance of the Liaw model and the ANN-based approach is systematically evaluated against experimental measurements using statistical error metrics, highlighting the strengths and limitations of each modeling strategy.

The hybrid Liaw–ANN model was applied to predict flash points for the eight binary mixtures in our dataset. The results are presented in comparison to experimental measurements and the pure Liaw–UNIFAC model predictions. Overall, the model captured both linear and non-linear flash point trends with high accuracy across all mixtures. The general performance is analyzed first and then delve into specific behaviors observed in different mixture classes, highlighting physical interpretations and model advantages.

3.1 Flash Point Behavior of Binary Mixtures. - The experimental flash point behavior of the investigated binary mixtures reflects the combined effects of component volatility, molecular interactions, and solution non-ideality. By examining different mixture classes, clear trends emerge that help interpret the observed composition-dependent flash point variations.

3.1.1 Alcohol–Alcohol Mixtures. - Alcohol–alcohol systems such as 1-butanol + 2-butanol and ethanol + 2-butanol exhibit near-ideal behavior due to their similar molecular structures and hydrogen-bonding capabilities. The flash point varies almost linearly between the pure-component values, with only slight positive deviations. In Figure II(a),the experimental flash point data for the 1-butanol + 2-butanol binary system exhibit a monotonic and nearly linear increase with increasing mole fraction of the higher–flash point component. Since both components are structural isomers with identical molecular formulas but different hydroxyl group positions, the observed trend is primarily governed by subtle differences in molecular structure rather than large volatility contrasts. At low mole fractions, the mixture behavior is dominated by the component with relatively higher volatility, resulting in lower flash point values. As the composition shifts toward the less volatile isomer, the overall vapor pressure of the liquid phase decreases, leading to a gradual increase in flash point.

The absence of curvature anomalies or flash point extrema across the entire composition range indicates that the 1-butanol + 2-butanol system exhibits near-ideal mixing behavior from a flammability perspective. The similarity in molecular size, polarity, and hydrogen-bonding capability of the two isomers results in comparable intermolecular interactions in the liquid phase, minimizing excess Gibbs energy effects. Consequently, the flash point variation is largely dictated by linear blending of component volatilities rather than strong non-ideal interactions.

The Liaw model combined with UNIFAC activity coefficients successfully reproduces the experimentally observed trend, demonstrating good predictive performance throughout the composition range. Small deviations are observed at low to intermediate mole fractions, where the model slightly underestimates the flash point. This deviation may be attributed to limitations of the UNIFAC model, particularly in representing strong polarity differences between components. These discrepancies may arise from limitations of the UNIFAC group-contribution method in distinguishing subtle structural effects associated with hydroxyl group positioning in alcohol isomers. Since UNIFAC parameters are primarily developed for functional group contributions rather than positional isomerism, minor inaccuracies in activity coefficient estimation are expected. Nevertheless, the Liaw–UNIFAC approach captures the essential thermodynamic behavior of the system and remains suitable for engineering-level flash point estimation.

Similarly, in Figure II(b), the experimental flash point data for the ethanol + 2-butanol system exhibit a smooth, non-linear decrease with increasing mole fraction of 2-butanol, indicating a composition-dependent enhancement in mixture flammability. At low mole fractions, the flash point remains relatively high due to the dominance of ethanol, whose strong hydrogen-bonding interactions suppress vapor-phase flammability. As the mole fraction increases, these interactions weaken and the contribution of the more volatile and flammable component becomes significant, resulting in a progressive reduction in flash point. The absence of a local minimum across the entire composition range suggests near-ideal mixing behavior from a fire-safety standpoint, with no azeotropic flash point depression observed. A comparable monotonic trend is evident in the second binary system considered, confirming that volatility changes rather than abrupt thermodynamic anomalies govern the flash point behavior.

The Liaw model coupled with UNIFAC activity coefficients successfully reproduces the overall experimental trend across the full composition range. However, minor deviations are observed, particularly in the intermediate composition region ($x \approx 0.3–0.6$), where the model slightly overpredicts or underpredicts the flash point relative to experimental values. These discrepancies can be attributed to limitations in the UNIFAC group-contribution framework, which may not fully capture specific hydrogen-bonding effects between short-chain and branched alcohols, as well as the assumption of ideal vapor-phase behavior inherent in the Liaw formulation. Given the exponential sensitivity of flash point to vapor pressure and flammability limits, even small inaccuracies in activity coefficients can lead to noticeable deviations. Nevertheless, the Liaw–UNIFAC approach remains a reliable and physically interpretable method for preliminary safety evaluation.

In contrast, the artificial neural network predictions show excellent agreement with experimental data throughout the entire composition range. The ANN accurately tracks both the magnitude and curvature of the flash point variation, including the mid-composition region where the Liaw–UNIFAC model exhibits maximum deviation. This improved performance reflects the ANN's ability to learn complex non-linear relationships between composition and flash point without relying on simplifying thermodynamic assumptions. By implicitly accounting for combined effects of non-ideality, vapor pressure interactions, and flammability constraints, the ANN minimizes systematic error propagation commonly associated with mechanistic models.

3.1.2 Alcohol–Alkane Mixtures. - Alcohol–alkane mixtures, including 2-butanol + n-octane and 1-butanol + n-octane, exhibit pronounced non-ideal behavior arising from strong polarity differences between the components. The experimental flash point data presented in Figure II(c) and Figure II(d) show a distinctly non-linear dependence on composition, characterized by an initial plateau or slight decrease at low alcohol mole fractions, followed by a pronounced increase at higher alcohol concentrations. At alkane-rich conditions, the flash point remains close to that of n-octane, reflecting the dominance of the nonpolar component in governing vapor-phase flammability.

In the low alcohol concentration region, the alcohol molecules experience unfavorable interactions with the alkane-rich liquid phase, resulting in activity coefficients significantly greater than unity. This positive deviation from Raoult's law enhances the partial vapor pressure of the alcohol, increasing the concentration of flammable vapor above the liquid surface. As a result, the flash point is depressed relative to ideal mixture predictions despite the higher intrinsic flash point of the alcohol. This effect is more evident for 2-butanol + n-octane, where steric hindrance around the hydroxyl group further weakens hydrogen bonding in the nonpolar environment, intensifying non-ideal vaporization behavior.

As the alcohol mole fraction increases, the liquid-phase structure gradually transitions toward alcohol-dominated intermolecular interactions. Hydrogen bonding between alcohol molecules becomes more prevalent, reducing overall volatility and suppressing the vapor pressure of the mixture. Simultaneously, the alkane component becomes increasingly destabilized within the polar-rich matrix, contributing less effectively to the vapor phase. These combined effects lead to a rapid increase in flash point at higher alcohol concentrations, producing the concave-upward flash point curves observed experimentally in both systems.

The Liaw–UNIFAC model captures the general shape of the experimental flash point curves but exhibits noticeable deviations in the intermediate composition range. These discrepancies arise from the difficulty of group-contribution methods in accurately representing strong polarity-driven non-idealities and composition-dependent activity coefficients in alcohol–alkane systems. While the Liaw–UNIFAC framework successfully reflects the competing effects of enhanced alcohol volatility at low mole fractions and volatility suppression at high mole fractions, it tends to smooth sharp transitions in flash point behavior.

In contrast, the artificial neural network predictions show excellent agreement with experimental data across the entire composition range for both systems. The ANN accurately reproduces the initial flash point depression, the shallow minimum region, and the subsequent sharp increase at higher alcohol contents. This superior performance highlights the ANN's ability to implicitly learn complex polar–nonpolar interaction effects, including non-linear activity coefficient behavior, without reliance on simplifying thermodynamic assumptions.

3.1.3 Alkane–Aromatic Mixtures. - Mixtures composed of non-polar hydrocarbons, such as n-heptane + o-xylene and ethylbenzene + n-heptane, exhibit behavior that is close to ideal, as both components interact predominantly through dispersion forces with minimal specific intermolecular interactions. The experimental flash point data presented in Figure II(e) and Figure II(f) show an almost linear decrease with increasing mole fraction of n-heptane, reflecting a gradual transition from the higher-flash-point aromatic component to the more volatile alkane.

In the n-heptane + o-xylene system, a slight negative deviation from linearity is observed, particularly in the aromatic-rich region. This behavior suggests weak repulsive interactions between unlike molecules, which marginally increase the escaping tendency of the components and lead to a small enhancement in mixture volatility. Consequently, the flash point decreases slightly faster than predicted by ideal mixing. However, the magnitude of this deviation remains small, indicating that excess Gibbs energy effects are minimal and that Raoult's law provides a reasonable first-order description of the system.

A similar trend is observed for the ethylbenzene + n-heptane mixture, where the flash point decreases smoothly with composition and closely follows ideal mixture predictions. The structural similarity and comparable non-polar character of the components result in nearly uniform intermolecular environments across the composition range, suppressing strong non-ideal behavior. As a result, the flash point variation is governed primarily by the relative volatilities of the pure components rather than by composition-dependent activity coefficient effects.

The Liaw–UNIFAC model accurately reproduces the near-linear experimental trends for both systems, with only minor discrepancies at intermediate compositions. These small deviations can be attributed to uncertainties in group-contribution parameters and the cumulative sensitivity of flash point calculations to vapor pressure estimates. Nevertheless, the model effectively captures the dominant physical behavior of these nearly ideal mixtures.

The artificial neural network predictions show excellent agreement with experimental data across the entire composition range, accurately reproducing both the slope and magnitude of the flash point–composition relationship. While the improvement over the thermodynamic model is less pronounced than in strongly non-ideal systems, the ANN still provides marginally enhanced accuracy, particularly in regions where subtle deviations from ideality are present.

3.1.4 Ketone–Alkane Mixture. - The acetone + n-decane system exhibits strongly non-linear flash point behavior due to the extreme contrast in volatility and polarity between the components. Acetone, characterized by a very low flash point and high vapor pressure, exerts a dominant influence on mixture flammability even at low mole fractions. As observed experimentally in Figure II(g), the flash point decreases sharply with the initial addition of acetone, highlighting the disproportionate contribution of the low-flash-point component to the vapor phase.

In the decane-rich region, acetone molecules experience weak stabilizing interactions within the nonpolar hydrocarbon matrix, resulting in activity coefficients significantly greater than unity. This positive deviation from Raoult's law markedly enhances the partial vapor pressure of acetone, leading to a rapid enrichment of flammable vapor above the liquid surface and a pronounced reduction in flash point. Consequently, the flash point depression is much steeper than would be expected from ideal mixing, underscoring the sensitivity of mixture flammability to small amounts of highly volatile polar solvents.

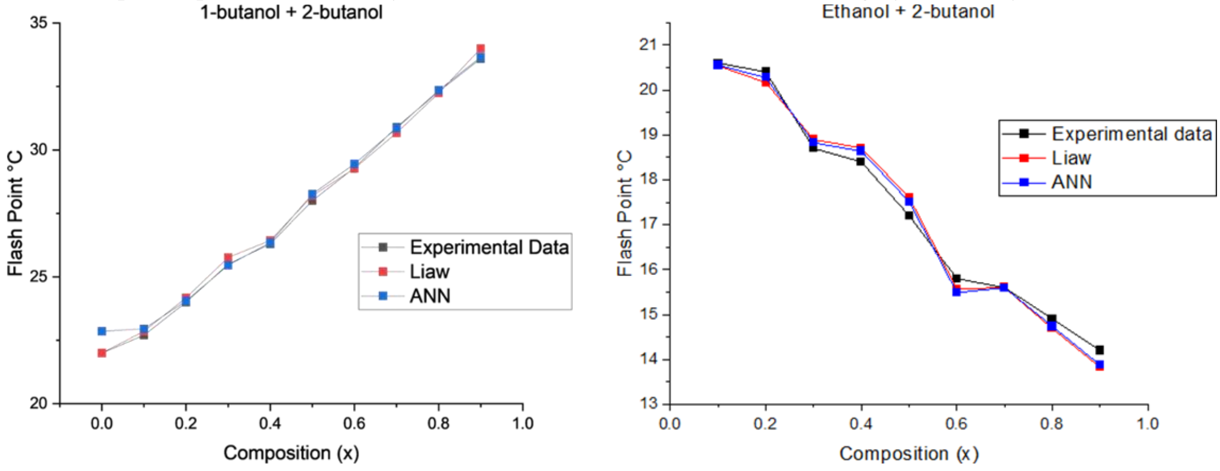
As the acetone mole fraction increases further, the liquid-phase behavior transitions toward acetone-dominated interactions. Although n-decane becomes increasingly destabilized in the polar-rich environment, its contribution to the vapor phase remains limited due to its inherently low volatility. At high acetone concentrations, the flash point rises sharply toward that of pure acetone, producing the strongly asymmetric flash point–composition curve observed experimentally. This behavior reflects the shift from alkane-controlled to acetone-controlled flammability regimes.

The Liaw–UNIFAC model captures the general trend of strong non-linearity but exhibits noticeable deviations in regions where the activity coefficient of acetone changes rapidly with composition. These discrepancies arise from limitations of group-contribution methods in accurately representing extreme polarity contrasts and large positive deviations from ideality. In particular, the model tends to smooth the sharp transition observed experimentally at high acetone mole fractions.

In contrast, the artificial neural network predictions closely match the experimental flash point data across the entire composition range. The ANN accurately reproduces the steep initial flash point depression, the intermediate plateau region, and the sharp rise at high acetone concentrations. This superior performance demonstrates the ANN's ability to learn highly non-linear composition–flammability relationships driven by extreme volatility differences without reliance on simplifying thermodynamic assumptions. It should be noted that the interpretations presented are based on observed trends, and direct validation through activity coefficient comparison or additional thermodynamic analysis would be required for definitive conclusions.

3.1.5 Additional System. - The n-heptane + o-xylene mixture exhibits near-ideal behavior, as indicated by the almost linear decrease in flash point across the entire composition range in Figure II(h). The flash point decreases steadily from approximately 32 °C for pure o-xylene to about −4 °C at high n-heptane mole fractions, reflecting the progressive dominance of the more volatile alkane component. The absence of pronounced curvature or extrema suggests that intermolecular interactions are governed primarily by dispersion forces, resulting in activity coefficients close to unity throughout the composition range. Both the Liaw–UNIFAC and ANN predictions closely follow the experimental trend, with only minor deviations at intermediate compositions, confirming the suitability of this system as a benchmark for evaluating model consistency under near-ideal mixing conditions.

Small residual discrepancies between model predictions and experimental data may partly reflect experimental scatter inherent to flash point measurements, particularly near composition extremes. Such uncertainty is well documented for closed-cup flash point tests and may contribute to the observed deviations in highly volatile systems.



(a) (b)

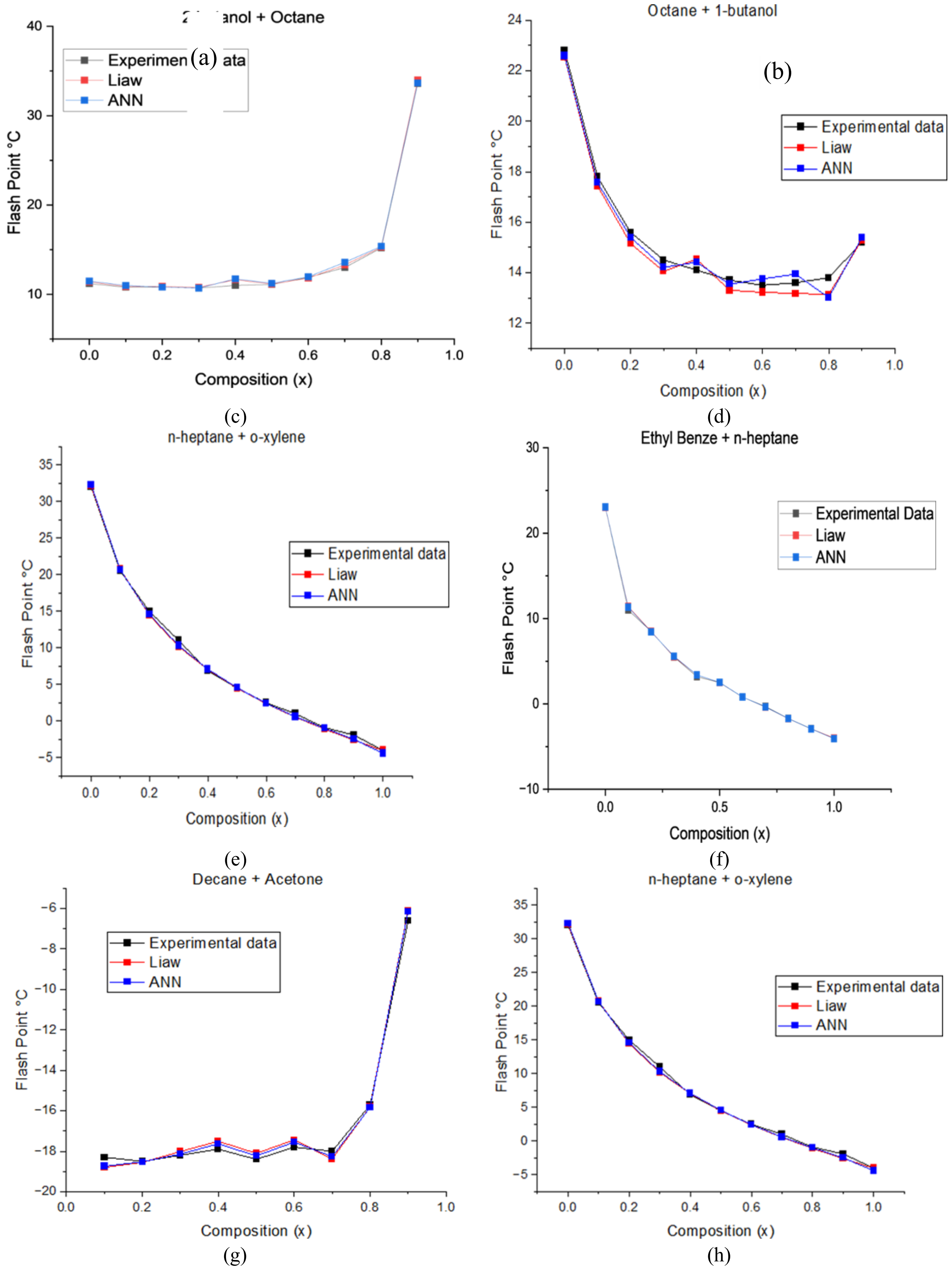


Figure II. Experimental and predicted flash points of binary mixtures using the Liaw–UNIFAC model and ANN.points for the eight investigated binary systems.

3.2 Model Performance and Comparison with the Liaw–UNIFAC Model. - The predictive performance of the Liaw–UNIFAC and ANN models was evaluated against experimental flash point data for eight binary mixtures spanning alcohol–alcohol, alcohol–ketone, alcohol–alkane, aromatic–alkane, and ketone–alkane systems as depicted in Figure III. For the decane + acetone mixture, both models accurately reproduce the nearly flat flash point profile at low acetone concentrations followed by a sharp rise at higher compositions, with the ANN providing a slightly smoother transition near the inflection region. In the ethanol + 2-butanone system, the flash point decreases monotonically with increasing ethanol fraction due to enhanced volatility and non-ideal interactions; here, the ANN demonstrates closer agreement with experimental values than the Liaw model, particularly at intermediate compositions. The alcohol–alcohol system (1-butanol + 2-butanol) exhibits near-ideal behavior, for which both models show almost perfect overlap with experimental data across the entire composition range.

For the 2-butanol + n-octane mixture, characterized by strong non-ideality, both models capture the pronounced curvature in flash point behavior, with the ANN yielding a smoother fit and marginally improved accuracy. In the n-heptane + o-xylene system, which presents a large disparity in component volatilities, the predicted flash points from both models closely track experimental trends, while the ANN predictions exhibit near-complete overlap with measured values. Similar agreement is observed for the octane + 1-butanol system, where a non-linear profile with a shallow minimum at intermediate compositions is more accurately reproduced by the ANN than by the thermodynamic model. For the remaining mixtures shown in the figure, including those exhibiting weak composition dependence and those with pronounced non-linear trends, both approaches perform satisfactorily; however, the ANN consistently demonstrates enhanced robustness in capturing subtle deviations from ideality. Overall, across all eight binary systems, the ANN model matches or slightly outperforms the Liaw–UNIFAC model, particularly for mixtures exhibiting strong non-ideal behavior, confirming its suitability as a reliable data-driven alternative for flash point prediction.

3.3 Quantitative Performance Evaluation Across All Binary Mixtures. - To evaluate the predictive capability of the proposed modeling framework, the performance of the Liaw–UNIFAC model and its ANN-enhanced variant was systematically assessed against experimental flash point data for a wide range of binary mixtures using statistical metrics such as the coefficient of determination (R^2) and mean squared error (MSE) as shown in Figure III and IV. Across all investigated binary mixtures, the Liaw–UNIFAC model shows strong agreement with experimental flash point data, with coefficients of determination (R^2) ranging from 0.983 to 0.9988.Excellent performance is observed for chemically similar and weakly non-ideal systems, such as 1-butanol + 2-butanol ($R^2 = 0.9928$, MSE = 0.0778) and hydrocarbon–aromatic mixtures ($R^2 > 0.997$), confirming the robustness of the thermodynamic framework for such systems. Higher deviations are primarily associated with strongly non-ideal polar–nonpolar mixtures, including ethanol + 2-butanol and octane + 1-butanol, where increased activity coefficient uncertainty leads to larger errors. Incorporation of the ANN consistently improves predictive accuracy across nearly all mixtures, yielding near-unity correlations (R^2 = 0.980–0.9999) and substantial reductions in MSE.

The most pronounced improvements occur for highly non-ideal systems, where error reductions of up to two orders of magnitude are achieved (e.g., ethanol + 2-butanol: MSE reduced from 0.28 to 0.0046). With the exception of octane + 1-butanol, where residual deviations likely reflect experimental scatter the ANN preserves thermodynamic trends while significantly enhancing numerical precision. Overall, the ANN functions as a robust thermodynamically informed surrogate model, delivering superior accuracy for complex mixtures while maintaining physical consistency. In addition to the previously reported performance metrics, Figure the mean absolute error (MAE) and root mean squared error (RMSE) were evaluated to provide a quantitative measure of prediction accuracy. For the comparison between experimental and Liaw-predicted flash point values, the MAE ranged from 0.071 (n-heptane + ethylbenzene) to 0.521 (octane + 1-butanol), while the corresponding RMSE ranged from 0.142 to 0.621, indicating that the Liaw model provided reasonably close predictions across most binary systems.

When comparing the Liaw model outputs against ANN predictions, the MAE and RMSE values were consistently lower, ranging from 0.027 to 0.260 and 0.041 to 0.341, respectively, demonstrating that the ANN successfully learned and reproduced the Liaw model behavior with high fidelity. The relatively small error magnitudes across all eight binary systems confirm the reliability of both modeling approaches in estimating flash points of flammable liquid mixtures. Figure V presents residual plots defined as predicted minus experimental flash point (°C) ,for both models across all binary mixture systems. For the Liaw–UNIFAC model, residuals are largely confined within the ±1°C band, with minor systematic scatter observed in the intermediate temperature range (0°C to 20°C), particularly for mixtures exhibiting stronger thermodynamic non-ideality such as ethanol + 2-butanol and n-octane + 1-butanol. The ANN residual plot demonstrates a comparable spread but with a marginally more uniform distribution about the zero-residual line, indicating reduced systematic bias.

Leakage diagnostics were performed to ensure the integrity of the dataset splitting procedure. Each datapoint was encoded using SHA-256 based on all input features, and the resulting hashes were compared across the training, validation, and test sets. No overlap was observed, confirming that no identical datapoints were present across different splits. In addition, near-duplicate detection was conducted by rounding all input features to three decimal places prior to hashing; this analysis also revealed zero overlap, ensuring strict separation and eliminating the possibility of data leakage. To evaluate the independent predictive capability of the model, an ablation study was performed. The Liaw correlation alone achieved an R^2 of 0.9993, indicating strong predictive performance. The ANN model trained without the Liaw feature achieved an R^2 of 0.9981, demonstrating that the model is capable of independently learning the underlying nonlinear relationships governing flash point behavior. When the Liaw prediction was included as an input feature, the model achieved an R^2 of 0.9995. Although the improvement is modest, it consistently enhances predictive accuracy, suggesting that the ANN utilizes the Liaw correlation as a complementary input while capturing residual nonlinearities not fully represented by the correlation itself. A detailed statistical breakdown of model performance, including per-mixture metrics, split-wise evaluation, and uncertainty quantification (e.g., mean ± standard deviation across repeated runs), was not fully explored in this study due to dataset limitations. Future work will incorporate such analyses to provide a more comprehensive assessment of model robustness.

Due to the composition-dependent nature of mixture data, random data splitting may introduce correlations between training, validation, and testing subsets. Therefore, the reported performance primarily reflects interpolation capability within the studied systems rather than strict extrapolation. Since the ANN incorporates Liaw–UNIFAC predictions as part of the input space, its performance primarily reflects correction and interpolation within the studied mixture systems. Therefore, extrapolation to entirely unseen mixture systems requires further validation and is identified as a direction for future work. It should be noted that the use of a constant LFL value represents a simplifying assumption. In reality, the flammability limit may vary with composition and component type, and incorporating composition-dependent or component-specific LFL values could further improve prediction accuracy.

A more rigorous validation strategy, such as leave-one-mixture-out or leave-one-system-out validation, would provide a stronger assessment of the model's ability to generalize to entirely unseen binary pairs. This remains an important direction for future work.

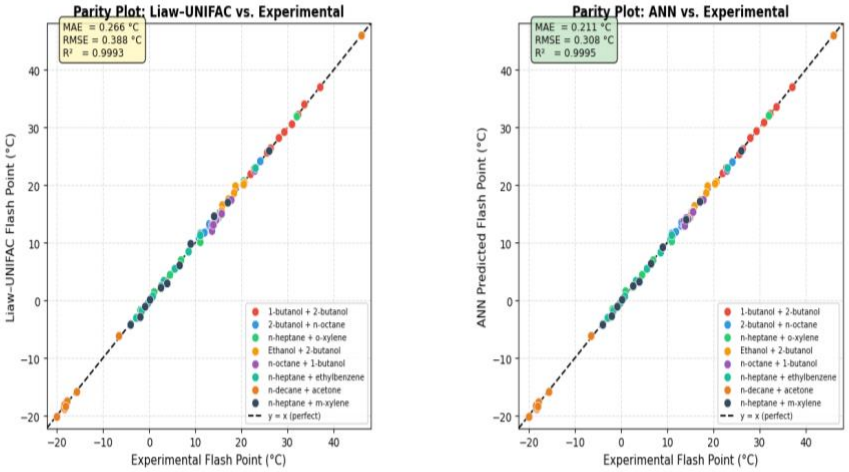


Figure III. R^2 plot comparing experimental flash points with Liaw–UNIFAC predictions and ANN-based estimates for eight binary mixtures.

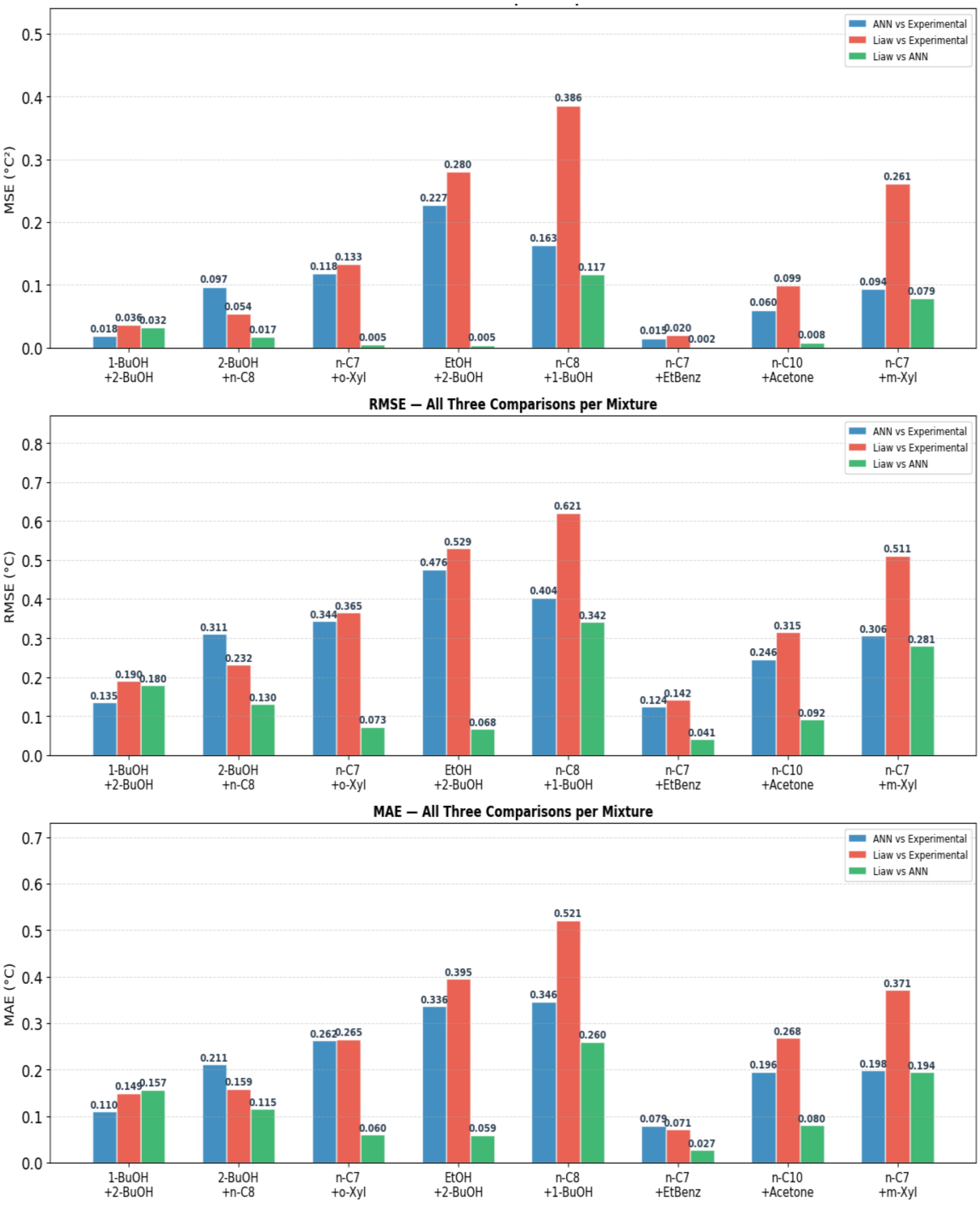


Figure IV. MSE, RMSE and MAE plots for ANN and Liaw UNIFAC.

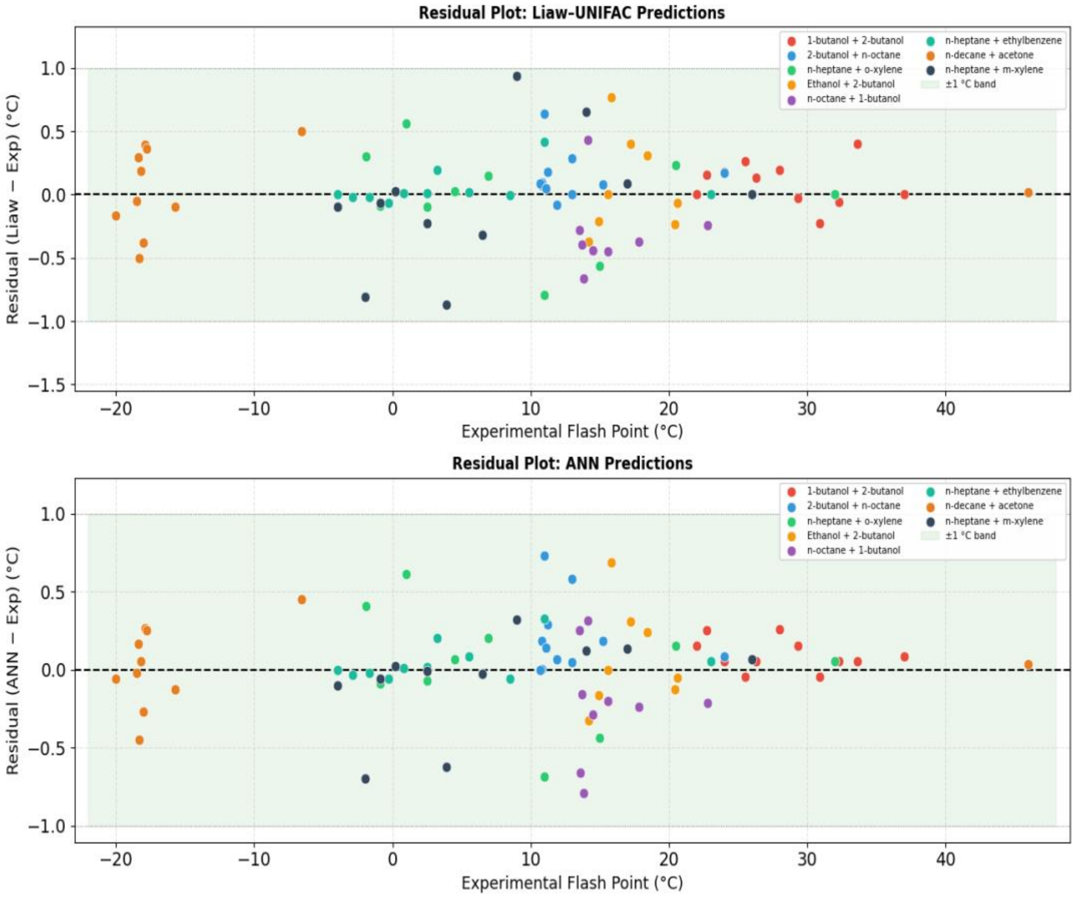


Figure V. Residual plots for ANN and Liaw Predictions.

The applicability of the proposed hybrid modeling framework is limited to the range of binary mixtures and chemical families included in the training dataset. Systems exhibiting strong association effects (e.g., hydrogen bonding beyond simple alcohol systems) or partial miscibility may present additional challenges due to complex phase behavior not fully captured by the current thermodynamic–ANN formulation. Furthermore, the model's predictive capability primarily reflects interpolation within the studied chemical space and may not directly extend to entirely new mixture types without additional training data.

In addition, the accuracy of flash point predictions is inherently sensitive to key thermodynamic inputs, including Antoine vapor pressure parameters and the assumed lower flammability limit (LFL). Uncertainty in these parameters, as well as the use of simplified assumptions such as constant LFL values, may contribute to deviations between predicted and experimental results.

4. Implication of this study. - Accurate flash point prediction has significant implications in chemical process safety, fuel blending, and regulatory compliance. The developed ANN-based model can be utilized as a decision-support tool in several ways:

- Safety Engineering: During early design of chemical processes or storage facilities, engineers can quickly screen the flammability of various solvent mixtures using the model. This enables safer selection of solvents and process conditions without waiting for exhaustive lab flash point measurements. For instance, if considering a solvent swap in a reaction, the model can predict if the new solvent mixture would have a higher or lower flash point and thus higher or lower fire risk. By integrating the model into process simulators, dynamic updates of stream flash points can warn operators of hazardous conditions in real-time.

- Fuel Blending and Alternative Fuels: The push for biofuels and blended fuels (ethanol/gasoline, biodiesel/diesel, etc.) requires that new formulations meet safety standards, one of which is a minimum flash point for transport fuels (e.g. diesel must typically have flash point > 52 °C by regulation). Our model can aid fuel chemists in formulating blends that maintain acceptable flash points. For example, if adding an oxygenated additive to diesel to improve emissions, the model can predict how much of the additive can be included before the flash point drops below the regulatory threshold. This prevents trial-and-error and ensures regulatory compliance is considered at the design stage. The model's success with hydrocarbon+oxygenate mixtures (like decane+acetone, butanol+octane) showcases its relevance in fuel contexts.

- Incident Investigation and Risk Assessment: When analyzing incidents or near-misses involving flammable mixtures, knowing the mixture's flash point is crucial. If an exact composition is uncertain, the model can be run for a range of plausible compositions to estimate the flash point range, helping investigators understand if a mixture was above or below its flash point under operating temperatures. Similarly, in Quantitative Risk Assessments (QRAs), the model can provide flash point data for various mixtures present in a facility, feeding into calculations of ignition probabilities and hazardous area classifications.

- Scale-Up and Storage Guidelines: In pilot plants or scale-up, mixtures might arise (e.g. waste solvent cocktails, or reactor byproducts) for which flash point data aren't readily available. The ANN model can fill this gap by predicting flash points on the fly, ensuring that appropriate storage (closed container, inert atmosphere, refrigeration if needed) and handling procedures (bonding, grounding, ventilation) are implemented. This is aligned with the trend of using digital tools for safety – having a computational "flash point advisor" can strengthen process safety management by reducing unknowns.

- Regulatory and Compliance Applications: Regulatory bodies could use models like this as part of classifying substances in hazard communication standards. While experimental determination is still the gold standard for official classification, a model that is proven accurate could be accepted for mixtures that are hard to test (toxic or explosive mixtures where standard flash point apparatus cannot be used safely). This would expedite compliance with transport and storage regulations for new chemical products.

In practical use, it should be emphasized to the end-user that the model provides estimates and not absolute truths. A safety margin (say 5–10 °C above the predicted flash point) might be advisable when using the predictions for critical decisions, to account for any uncertainties. Nonetheless, given the high accuracy demonstrated (often within 1 °C of actual), the model can be confidently used for most engineering purposes, dramatically reducing the need for extensive empirical testing during formulation and design stages.

4. Conclusion. - This study demonstrates the effectiveness of integrating thermodynamically grounded modeling with machine learning for accurate flash point prediction of liquid mixtures. By embedding Liaw–UNIFAC–derived physical descriptors into an ANN framework, the proposed hybrid model achieves high predictive accuracy (≈1 °C average error) across a wide range of binary systems, including both near-ideal and strongly non-ideal mixtures. The incorporation of activity coefficients and vapor pressure parameters ensures thermodynamic consistency, enabling the ANN to preserve physical trends and remain within realistic flash point bounds.

Once trained, the model delivers rapid predictions at negligible computational cost, making it well suited for large-scale process simulations and early-stage solvent or mixture screening. While the present work focuses on binary mixtures, the methodology is readily extensible to more complex multicomponent systems through expanded datasets and advanced network architectures. Overall, this hybrid approach provides a reliable and computationally efficient tool for process safety assessment, supporting inherently safer design and highlighting the broader potential of physics-informed machine learning for safety-critical property prediction in chemical engineering

Data Availability Statement. - All data supporting the findings of this study, including the binary mixture flash point dataset and input parameters (vapor pressure coefficients, UNIFAC group assignments), are available from the corresponding author upon reasonable request. Additionally, the compiled dataset and MATLAB scripts used for training and evaluating the ANN model have been uploaded as supplementary material with this manuscript.

Conflict of Interest. - The authors declare no conflict of interest.

Acknowledgments. - During the preparation of this work, the authors used ChatGPT 4.0 to refine writing and improve readability. The authors have reviewed and edited the AI-generated content as necessary and take full responsibility for the contents of this publication.

Nomenclature

- ANN: Artificial Neural Network
- ASTM: American Society for Testing and Materials (standard methods organization)
- FAEE: Fatty Acid Ethyl Ester (biodiesel component)
- FP (Flash Point): Lowest temperature at which a liquid's vapor ignites (in °C)
- LFL: Lower Flammability Limit (volume fraction of vapor in air, typically %)
- MSE: Mean Squared Error
- MAE: Mean Absolute Error
- RMSE: Root Mean Squared Error
- MaxFPB: Maximum Flash Point Behavior (phenomenon where a mixture's flash point is higher than both pure components)
- MinFPB: Minimum Flash Point Behavior (mixture flash point lower than both components)
- QSPR: Quantitative Structure–Property Relationship
- R^2: Coefficient of Determination (fraction of variance explained)
- UNIFAC: UNIversal Functional-group Activity Coefficient model (group contribution method for activity coefficients)
- γ_1: Activity Coefficient of Component 1
- γ_2: Activity Coefficient of Component 2
- x_1: Mole fraction of Component 1
- x_2: Mole fraction of Component 2
- (Note: All temperatures are in °C. Composition is given in mole fraction unless otherwise noted. Vapor pressures are in bar, and standard atmospheric pressure Patm = 1.013 bar.)

References

[1] C. Ding et al., "Experimental study and hazard analysis on the flash point of flammable liquids at high altitudes," Journal of Fire Sciences, vol. 31, pp. 469-477, 08/25 2013.

[2] D. C. Do Nascimento, N. D. D. Carareto, A. M. B. Neto, V. Gerbaud, and M. C. da Costa, "Flash point prediction with UNIFAC type models of ethylic biodiesel and binary/ternary mixtures of FAEEs," Fuel, vol. 281, p. 118717, 2020.

[3] H. Xiao, W. Wang, H. Bao, F. Li, and L. Zhou, "Biodiesel-diesel blend optimized via leave-one cross-validation based on kinematic viscosity, calorific value, and flash point," Industrial Crops and Products, vol. 191, p. 115914, 2023.

[4] J. Fu, "Flash points measurements and prediction of biofuels and biofuel blends with aromatic fluids," Fuel, vol. 241, pp. 892-900, 04/01 2019.

[5] B. Nazari, M. H. Keshavarz, and A. Hassanzadeh, "Reliable prediction of the flash point of organic compounds containing hazardous peroxide functional groups as compared to the best available methods," Process Safety and Environmental Protection, vol. 132, pp. 134-141, 2019.

[6] H.-J. Liaw, W.-C. Hsu, and K. Lakzian, "Exploration of two types of maximum–minimum flash point behavior of ternary mixtures," Journal of Loss Prevention in the Process Industries, vol. 80, p. 104915, 2022.

[7] Z. Heidari and M. A. Sobati, "New structure-based models for the prediction of flash point and autoignition temperatures of alkyl esters," Chemometrics and Intelligent Laboratory Systems, vol. 240, p. 104877, 2023.

[8] F. H. B. Sosa, F. A. Temoteo, R. M. Dias, D. C. do Nascimento, A. M. B. Neto, and M. C. da Costa, "Flash point of binary and ternary mixture of biojet blends: Experimental data and modeling," Fluid Phase Equilibria, vol. 576, p. 113940, 2024.

[9] S. M. Santos, D. C. Nascimento, M. C. Costa, A. M. B. Neto, and L. V. Fregolente, "Flash point prediction: Reviewing empirical models for hydrocarbons, petroleum fraction, biodiesel, and blends," Fuel, vol. 263, p. 116375, 2020/03/01/ 2020.

[10] H.-J. Liaw and C.-A. Yang, "Maximum flash point behavior of ternary mixtures with single and two maximum flash point binary constituents," Process Safety and Environmental Protection, vol. 143, pp. 293-303, 2020.

[11] K. Lakzian, S. Hosseiniallahchal, H. Jalaei Salmani, and A. Sanjarifard, "Flash point prediction of binary totally and partially miscible water-alcohol mixtures by cubic-plus-association (CPA) equation of state," Thermochimica Acta, vol. 691, p. 178719, 2020/09/01/ 2020.

[12] Z. Ke, H. Wu, C. Geng, G. Wang, Y. Yang, and Y.-W. Li, "A Comparative Study of PC-SAFT EOS and Activity Coefficient Models in Phase Equilibria Calculations for Mixtures Containing Associating and Polar Components," Industrial & Engineering Chemistry Research, vol. 57, 02/06 2018, doi: 10.1021/acs.iecr.7b04758.

[13] V. Koulocheris, M. Panteli, E. Petropoulou, V. Louli, and E. Voutsas, "Modeling of Simultaneous Chemical and Phase Equilibria in Systems Involving Non-reactive and Reactive Azeotropesi," Industrial & Engineering Chemistry Research, vol. 59, no. 18, pp. 8836-8847, 2020/05/06 2020, doi: 10.1021/acs.iecr.0c00468.

[14] M. P. de Omena Souza, D. C. do Nascimento, D. T. Volpatto, G. G. Ribeiro, A. M. B. Neto, and M. C. da Costa, "Modeling flash points of biofuels using neural networks," Fluid Phase Equilibria", vol. 596, p.114439, 2025, doi.org/10.1016/j.fluid.2025.114439.

[15] H. Jalaei Salmani, H. Kalani, M. R. Moradi, E. Mansouri, H.-J. Liaw, and H. Karkhanechi, "A practical hybrid machine learning method for predicting the flash point of complex ternary alcohol-based mixtures," Petroleum Science and Technology, vol. 42, no. 25, pp. 4390-4404, 2024, doi.org/10.1080/10916466.2023.2246489.

[16] B. Aljaman, U. Ahmed, U. Zahid, M. R. Vanteru, M. Sarathy, and A. G. Abdul Jameel, "A comprehensive neural network model for predicting flash point of oxygenated fuels using a functional group approach," Fuel, vol. 317, p. 123428, 06/01 2022, doi.org/10.1016/j.fuel.2022.123428.

[17] A. Álvarez, M. n. Lapuerta, and J. R. Agudelo, "Prediction of flash-point temperature of alcohol/biodiesel/diesel fuel blends," Industrial & Engineering Chemistry Research, vol. 58, no. 16, pp. 6860-6869, 2019, doi: 10.1021/acs.iecr.9b00843.

[18] Y. Pan, J. Cheng, X. Song, G. Li, L. Ding, and J. Jiang, "Flash points measurements and prediction for binary miscible mixtures," Journal of Loss Prevention in the Process Industries, vol. 34, pp. 56-64, 2015, doi.org/10.1016/j.jlp.2015.01.022.

[19] X. Huo, Q. Lu, and J. Wang, "Liaw-UNIFAC flash point model for alcohols-kerosene/diesel fuel blends using average fuel structure," Process Safety and Environmental Protection, 2022, doi.org/10.1016/j.indcrop.2022.115914.

[20] Z. Liu and X. Yang, "Insight of low flammability limit on sustainable aviation fuel blend and prediction by ANN model," Energy and AI, vol. 18, p. 100423, 2024, doi: 10.1016/j.egyai.2024.100423.
[21] H. Mirshahvalad, R. Ghasemiasl, and N. Raoufi, "A Neural Networks Model for Accurate Prediction of the Flash Point of Chemical Compounds," Iranian Journal Of Chemistry & Chemical Engineering-International English Edition, vol. 39, pp. 297-304, 11/10 2020, doi: 10.30492/ijcce.2019.35001.
[22] H.-J. Liaw and Q.-R. Tang, "Flash point prediction of binary mixtures of ionic liquid and flammable solvent," Journal of Loss Prevention in the Process Industries", vol. 96, p. 105631, 2025, doi.org/10.1016/j.jlp.2025.105631.
[23] R. C. Boehm, R. Parker, Z. Yang, S. Dooley, and J. S. Heyne, "Blend Prediction Model for Vapor Pressure of Jet Fuel Range Hydrocarbons," Sustainability, vol. 17, no. 21, p. 9612, 2025, doi.org/10.3390/su17219612.
[24] H.-J. Liaw, "Prediction of the influence of pressure on flash points of liquid fuels at sub-atmospheric pressure," Journal of Loss Prevention in the Process Industries, vol. 91, p. 105373, 2024/10/01/ 2024, doi.org/10.1016/j.jlp.2024.105373.
[25] D. b. Costa do Nascimento, M. c. P. d. O. Souza, L. d. O. Hentges, R. M. Dias, A. Marinho Barbosa Neto, and M. C. a. o. d. Costa, "Mixture flash point calculation: recent advances and a closer look at biodiesel," ACS Chemical Health & Safety, vol. 31, no. 1, pp. 22-43, 2024,doi.org/10.1016/j.fuel.2020.118717.
[26] F. H. B. Sosa, F. A. Temoteo, R. M. Dias, D. Costa do Nascimento, A. M. B. Neto, and M. C. da Costa, "Flash point of binary and ternary mixture of biojet blends: Experimental data and modeling," Fluid Phase Equilibria, vol. 576, p. 113940, 2024/01/01/ 2024, doi.org/10.1016/j.fluid.2023.113940.

Author contribution:
1. Conception and design of the study
2. Data acquisition
3. Data analysis
4. Discussion of the results
5. Writing of the manuscript
6. Approval of the last version of the manuscript

NK has contributed to: 1, 2, 3, 4, 5 and 6.
AS has contributed to: 1, 2, 3, 4, 5 and 6.
AJ has contributed to: 1, 2, 3, 4, 5 and 6.
AAZ has contributed to: 1, 2, 3, 4, 5 and 6.

Acceptance Note: This article was approved by the journal editors Dr. Rafael Sotelo and Mag. Ing. Fernando A. Hernández Gobertti.