BINARY MIXTURE FLAMMABILITY CHARACTERISTICS

FOR HAZARD ASSESSMENT

A Dissertation

by

MIGVIA DEL C. VIDAL VÁZQUEZ

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Approved by:

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ABSTRACT

Binary Mixture Flammability Characteristics for Hazard Assessment.

(August 2005)

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Chair of Advisory Committee: Dr. M. Sam Mannan

Flammability is an important factor of safe practices for handling and storage of liquid mixtures and for the evaluation of the precise level of risk. Flash point is a major property used to determine the fire and explosion hazards of a liquid, and it is defined as the minimum temperature at which the vapor present over the liquid at equilibrium forms a flammable mixture when mixed with air.

Experimental tests for the complete composition range of a mixture are time consuming, whereas a mixture flash point can be estimated using a computational method and available information. The information needed for mixture flash point predictions are flashpoints, vapor pressures, and activity coefficients as functions of temperature for each mixture component. Generally, sufficient experimental data are unavailable and other ways of determining the basic information are needed. A procedure to evaluate the flash point of binary mixtures is proposed, which provides techniques that can be used to estimate a parameter that is needed for binary mixture flash point evaluations.

Minimum flash point behavior (MFPB) is exhibited when the flash point of the mixture is below the flash points of the individual components of the mixture. The identification of this behavior is critical, because a hazardous situation results from taking the lowest component flash point value as the mixture flash point.

Flash point predictions were performed for 14 binary mixtures using various G^{ex} models for the activity coefficients. Quantum chemical calculations and UNIFAC, a theoretical model that does not require experimental binary interaction parameters, are

employed in the mixture flash point predictions, which are validated with experimental data. MFPB is successfully predicted using the UNIFAC model when there are insufficient vapor liquid data.

The identification of inherent safety principles that can be applied to the flammability of binary liquid mixtures is also studied. The effect on the flash point values of three binary mixtures in which octane is the solute is investigated to apply the inherent safety concept.

DEDICATION

To my parents

Mr. Miguel A. Vidal Maldonado and Mrs. Sylvia E. Vázquez Cordero

and my brother and sister

Mr. Miguel A. Vidal Vázquez and Mrs. Marieberta Vidal Vázquez

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

AIChE	American Institute of Chemical Engineers
AIT	Autoignition Temperature
ASTM	American Society of Testing and Materials
BLEVEs	Boiling Liquid Expanding Vapor Explosions
COSMO-RS	Conductor-like Screening Model for Real Solvents
DOT	Department of Transportation
EPA	Environmental Protection Agency
F&EI	Fire and Explosion Index
FPBICS	Flash Point Between Individual Components
GCS	Group Contribution Solvation
GCS	Group Contribution Solvation
LFL	Lower Flammable Limit
LTL	Lower Temperature Limit of Flammability
MD	Molecular Dynamics
MF	Material Factor
MFPB	Minimum Flash Point Behavior
MKOPSC	Mary Kay O'Connor Process Safety Center
NFPA	National Fire Protection Association
NRTL	Non-Random Two Liquids
OSHA	Occupational Safety and Health Administration
PVAMU	Prairie View A&M University
QM	Quantum Mechanics
QSPR	Quantitative Structure Property Relationships
UFL	Upper Flammable Limit
UNIFAC	UNIQUAC Functional-group Activity Coefficients
UNIQUAC	Universal Quasi Chemical
VLE	Vapor Liquid Equilibria

LIST OF SYMBOLS

a, b, and *c*	Constants for the correlation of the flash point as a function of the boiling point
A_i, B_i and C_i	Antoine parameters of compound i
A_i, B_i, C_i, D_i and E_i	Extended Antoine regression coefficients for compound i
a_{mn} and a_{nm}	UNIFAC interaction parameters between molecule m and n
G^{ex}	Excess Gibbs energy
G_{ij}	NRTL model parameter
$\sqrt[3]{G_b}$	Cubic root of the gravitational index
$HDCA$	Hydrogen donor charged solvent accessible surface area
LFL_i	Lower flammable limit of component i
l_i	Parameter of the UNIQUAC and UNIFAC models
M_R	Molecular weight divided by the number of atoms in the molecule
P	Ambient pressure
P_c	Critical pressure
P_i^{sat}	Vapor pressure at temperature T
$P_{i,fp}^{sat}$ (T_f)	Vapor pressure at the flash point temperature
Q_k	Surface area parameter in the UNIFAC model
R	Gas constant
R_k	Group volume parameter in the UNIFAC model
T_b	Boiling point temperature
T_c	Critical temperature
T_f	Flash point temperature
T_r	Reduced temperature
x_i	Liquid mole fraction of component i
X_m	mole fraction of group m in the mixture
y_i	Vapor mole fraction of component i

z	Coordination number in the UNIQUAC and UNIFAC models

Greek letters

ω	Acentric factor
γ^{∞}	Activity coefficient at infinite dilution
γ_i	Activity coefficient of component i
τ_{ij}	Binary interaction parameter in liquid activity coefficient models (Table 2)
ρ_i^0	Density of liquid i.
$\Delta G_{i/i}^{*sol}$	Free energy change of the solvation of solute i in solvent i
$\Delta G_{i/j}^{*sol}$	Free energy change of the solvation of solute i in solvent j
υ_i	Molar volume of component i in the Wilson model
α	NRTL parameter
$v_k^{(i)}$	Number of k groups present in species i;
Γ	Residual group contribution to activity coefficient in the UNIQUAC and UNIFAC models
σ	Screening charge density
Φ_i	Segment fraction
θ_m	Surface area fraction of group m
Ψ	UNIFAC model parameter
Λ	Wilson model parameter

CHAPTER I

INTRODUCTION

The importance of safety, risk assessment, and emergency planning for industrial incidents and the requirements of governmental agencies provide the impetus to search for better and accurate techniques for the prediction of critical properties that are used as measures of safety such as flash points. The flash point is the minimum temperature of a liquid at which the vapor present over the liquid forms a flammable mixture when mixed with air. It is also the parameter used by organizations such as the National Fire Protection Agency (NFPA) to categorize the flammability of a substance.

Flammability is an important factor of safe practices for handling and storage of liquid mixtures and for the evaluation of the precise level of risk. Different standard test methods[1-10] exist for the experimental evaluation of flash points of pure chemicals. However, most industries work with mixtures instead of pure chemicals. Some of the pertinent questions are, "Can we treat mixtures as pure compounds and use the available methodologies to evaluate the risk associated with it? Is it safe to take the lowest flash point value as the mixture flash point temperature?" The answer to these questions is generally **NO**. The behavior of mixtures can be quite different compared to their individual components, and making such assumptions can be very dangerous.

Flash points are available for most pure liquids, but the information for mixtures is very limited. For mixtures of flammable liquids, or more importantly, liquid mixtures containing both flammable and nonflammable constituents, the precise level of risk is more difficult to predict.

This dissertation follows the style and format of the *Journal of Chemical and Engineering Data.*

1.1 DEFINITION OF FLAMMABILITY CHARACTERISTICS

There is not a single parameter that defines flammability, but some of the relevant properties are: flash point (T_f), lower flammable limit (LFL), upper flammable limit (UFL), and autoignition temperature (AIT). The relationship among these properties is presented in Figure 1.
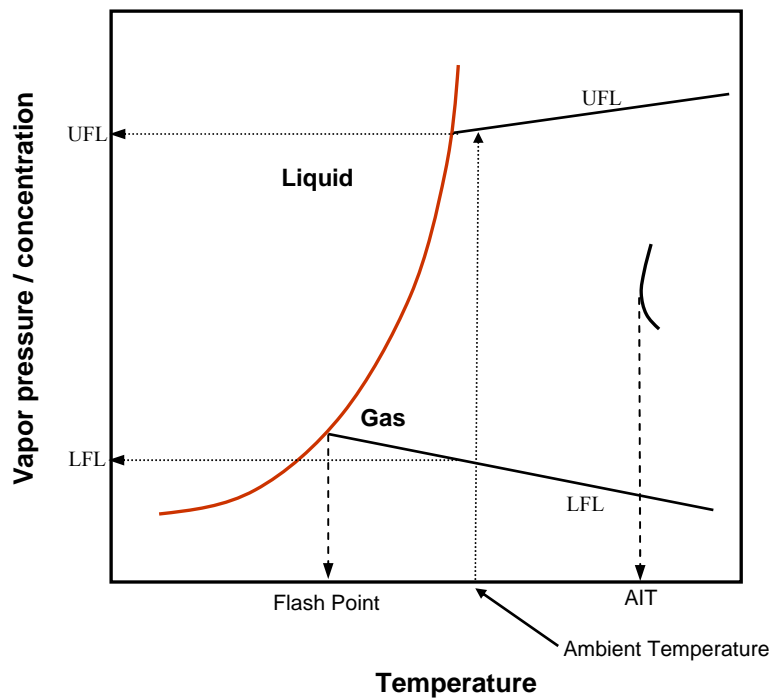
Figure 1. Relationship between different flammability properties.
(Adapted from BM Bull. 627[11])

The LFL and UFL are the minimum and maximum volumetric concentrations of fuel in air that set the endpoints of the flammability range. The LFL represents the initiating point of flame propagation, and the UFL represents the extinguishing point due

to the shortage of oxygen or excess of fuel. The AIT is the minimum temperature required to cause self-sustained combustion.[12]

The flash point of a flammable liquid is the temperature at which the vapor pressure of the liquid provides a concentration of vapor in air that corresponds to the LFL.[13] It is assumed that the flash point is the temperature at which the chemical generates enough vapor to be ignited. In reality, this temperature will be the fire point temperature, which is within a few degrees above the flash point temperature. However, the flash point criterion is used by regulatory authorities to rate the flammability hazards of chemicals. Based on these ratings, specific regulations and guidelines for usage, transportation, and storage are developed.

1.2 HAZARD ASSESSMENT

The major hazards with which the chemical industry is concerned are **fire**, explosion, and toxic release. Of these three, the most common is fire, but explosion is particularly significant in terms of fatalities and loss.[13] However, a fire can eventually lead to explosions such as: Boiling Liquid Expanding Vapor Explosions (BLEVEs) and vapor cloud explosions.

A hazardous material can be defined as a substance that poses an unacceptable risk to health, safety, or property. Absolute safety can never be achieved due to the inherent properties of some chemicals. Therefore, risk can only be reduced to an acceptable level. Hazards can be categorized by toxicity, reactivity, volatility, and combustibility or **flammability** of a substance.

Hazard assessment is a thorough, orderly, and systematic approach for identifying, evaluating, and controlling hazards of processes involving chemicals. There are many organizations that have developed lists, definitions, and classifications related to

flammable chemicals, including DOT, NFPA, OSHA, and EPA. Some organizations establish their classifications with qualitative descriptions but most classifications are based on physical/chemical properties such as **flash point (T_f)** and boiling point (T_b). The degrees of flammability according to NFPA and DOT are presented in Table 1.

1.3 STATEMENT OF THE PROBLEM

The flash point of a mixture can deviate considerably from the flash point values of the individual mixture components. This is the case of non-ideal mixtures which exhibits a minimum flash point behavior (MFPB). However, not all non-ideal mixtures belong to this group. Generally, in the industry, the flash point of the mixture is taken as the flash point of the mixture component with the lowest value. It is thought that this practice add a layer of protection, since the more "hazardous" compound is selected as the threshold value. This statement is supported by the following cited section of the NFPA 325[12]:

"Mixtures of two or more materials may have different hazard properties than any of the components. Although it is a common practice to base the fire hazard of a mixture on that of the most hazardous component, consideration should be given to testing the mixture itself."

Even though there are regulations and standards that use the flash point temperature as a criterion, most of the experimental standard test methods are for pure compounds. The flash point of a mixture is a function of the mixture composition. Therefore, a complete characterization of the liquid mixture is needed.

Table 1. Classification of Flammability According to DOT and NFPA

	Purpose	Flammability Definition	Classification		
DOT	Transportation Regulates transportation	Flammable liquid is any liquid with T_f < 141 ºF (60.5 ºC). Combustible liquid is any liquid with 141 ºF (60.5 ºC) < T_f < 200 ºF (93.3 ºC).	Class 3 flammable liquids are defined as liquids having a T_f of not more than 141 ºF (60.5 ºC) or any material in a liquid phase with a T_f at or above 100 ºF (37.8 ºC) .		

			NFPA 30 [a, b] Classification	NFPA 704[c] Hazard Rating	Liquid Definition
NFPA	Fire-fighting and fire protection	A liquid is classified as flammable if it has a T_f of 100ºF or lower, when tested by closed cup methods.	IA	4	T_f < 73 ºF (22.8 ºC) ; T_b < 100 ºF (37.8 ºC)
			IB, IC	3	T_f < 73 ºF (22.8 ºC); T_b ≥ 100 ºF (37.8 ºC) 100 ºF (37.8 ºC) > T_f ≥ 73 ºF (22.8 ºC)
	NFPA standard referenced by OSHA	Combustible liquids are those with T_f higher than 100 ºF (37.8 ºC)	II	2	140 ºF (60 ºC) > T_f ≥ 100 ºF (37.8 ºC)
			IIIA	2	200 ºF (93.3 ºC) ≤ T_f ≥ 140 ºF
			IIIB	1	T_f > 200 ºF (93.3 ºC)

[a] NFPA 30: Flammable and Combustible Liquids Code

[b] The OSHA classifications are the same as those in NFPA 30 (Scheffey *et al.*, 1996).[14]

[c] NFPA 704: Standard System for the Identification of the Fire Hazards of Materials

Prediction methods for the evaluation of the flash point of mixtures are desirable. Usually an estimated flash point value is needed when testing the flash point of mixtures. From a safety point of view, the knowledge of an estimated flash point value as close as possible to the real value can avoid incidents in the laboratory area. A simple mixing rule based on the composition of the mixture and on the flash point value of each component is sometimes used to estimate the flash point of the mixture. The flash point value obtained in this way is often fairly close to the flash point value of an ideal mixture. If the mixture is non-ideal, a mistakenly higher flash point value will be used as the flash point of the mixture. The standard test method ASTM E 1232[5] specifies that:

> "Care must be exercised in the use of estimated flashpoints for temperature limit testing of mixtures. There are many mixtures (non-ideal solutions) having flashpoints below the flashpoint of any component. Unless detailed data are available it is difficult to estimate temperature limits of flammability[a] of mixtures."

There are some models available for the prediction of the flash point of mixtures, but they are functions of some basic data and/or parameters. Due to the large quantity of chemicals manufactured as well as the infinite combination of mixtures, reliable prediction tools are needed to predict mixture flash point when experimental data are not available.

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[a] The temperature limit of flammability is the minimum temperature at which liquid chemicals evolve sufficient vapors to form a flammable mixture with air under equilibrium conditions.

1.4 OBJECTIVES

The objective of this work is the development of a systematic approach for the evaluation or prediction of the flash point of binary mixtures. The main goal is to identify the flash point of a binary mixture, especially those with MFPB, by incorporating several techniques that allow the reduction of experimental work without compromising process safety principles.

The mixture flash point prediction procedure is based on the currently available methods for prediction of flash points, vapor pressures of pure compounds, and activity coefficients for the components of the mixture. A general procedure that collects most of the available methods will provide the user with different alternatives to consider depending on the individual components of the mixture. Special attention has been given to the prediction capabilities of UNIFAC due to its wide application in the chemical industry. However, methodologies such as computational chemistry have also been considered.

The prediction capabilities of the procedure developed will be tested with aqueous and flammable binary mixtures. Based on the results, recommendations of when the assumption of selecting the most hazardous mixture component as a basis for the mixture flash point are given.

1.5 ORGANIZATION OF DISSERTATION

This dissertation is a result of a collaborative work between Mary Kay O'Connor Process Safety Center (MKOPSC) at Texas A&M and Prairie View A&M University (PVAMU). The theoretical work was developed at MKOPSC, while the experimental work was performed at PVAMU. The first chapter of this dissertation presents the gap between the existing regulations and the needs of the chemical industry. The intention behind regulations such as OSHA and DOT is to protect and preserve health and safety. However, some of the accepted test methods are not intended or suitable for mixtures, which cover most of the chemicals handled in the industry. Then, is it acceptable to perform a hazard assessment where the hazard is identified with approximate methods that sometimes are valid? Following that discussion, the objectives of this work are presented.

Experimental and predictive methodologies to test and evaluate the flash point of pure compounds and mixtures are discussed in Chapter II. The difference between an ideal and a non-ideal mixture and its implication in the flash point of the mixture are also covered in Chapter II. In addition, a brief introduction of the usefulness of computational chemistry to estimate activity coefficients and binary interaction parameters when insufficient experimental data are available is given.

The main product of this work is presented in Chapter III, which is the procedure for the prediction of the flash point of binary mixtures. The procedure highlights the basic data needed to estimate the mixture flash point. Different prediction and/or estimation methods to obtain that basic data are presented together to give the user alternatives according to the special characteristics of the mixture in evaluation. A screening methodology based on Liaw's rules[15] is used in combination with computational chemistry to predict mixtures exhibiting MFPB.

Flash point predictions for different aqueous and flammable binary mixtures are presented in Chapter IV. The predictions are compared with experimental data available in the literature or taken at PVAMU.

In Chapter V the concept of inherent safety is introduced. This chapter is intended to take the user to the next step of the hazard assessment. In Chapter IV, the hazard was identified and evaluated. Now it is time to control or reduce the hazard. Is it possible to modify the flash point of a mixture? The answer to this question is presented in Chapter V.

Chapter VI contains a compilation of conclusions and suggestions for future work.

CHAPTER II

BACKGROUND*

The first part of this chapter will discuss the experimental methods available to identify and test the flash point of a substance. The experimental part will cover most of the standard test methods accepted by OSHA and DOT regulations.

The second part will include the theoretical methods available to evaluate and estimate flash points. It covers the prediction models and correlations available to estimate the flash point of pure compounds and binary mixtures. Aqueous and flammable binary mixtures are the types of mixture considered. An aqueous binary mixture contains water and a flammable compound. In a flammable binary mixture both components are flammable. An introduction of MFPB is presented in the third part of this chapter.

The fourth part explains the excess Gibbs (G^{ex}) models available to obtain the activity coefficients, which are extremely important for the prediction of mixture flash point. Since the activity coefficients cannot be measured experimentally, the advantages and limitations of these models are briefly reviewed. Computational chemistry as an alternative to obtain activity coefficients at infinite dilution is discussed.

2.1 FLASH POINT EXPERIMENTAL METHODS

Flash points are determined experimentally by heating the liquid in a container and then introducing a small flame just above the liquid surface. The temperature at which there is a flash/ignition is recorded as the flash point.[16] Two general experimental methods are the closed cup and open cup. In the closed cup method the fuel is enclosed, while in the open cup the fuel is exposed to open air. The flash points determined with the closed cup method are usually lower than the open cup method values because the vapors are prevented from escaping.

A review of the closed cup standard test methods are presented in ASTM E 502.[1] The difference between ASTM D 93[8] and ASTM D 56[7] is the experimental apparatus. In the ASTM D 93 a Pensky Closed Cup tester is required, which contains a stirring device and the ASTM D 56 utilizes a Tag Closed Tester with no stirring. In both ASTM D 93 and ASTM D 56 a rate of heating is applied for the material under test. The experimental data taken at PVAMU was obtained using the Pensky Closed Cup tester in Figure 2.

Figure 2. Closed cup tester used at PVAMU.

The ASTM D 3941[2] is a closed cup method that uses a slower heating rate than the ASTM D93[8] and D 56[7] methods and is intended for low thermal conductivity liquids.

The ASTM E 1232 method is intended to measure the lower temperature limit of flammability (LTL), which is the minimum temperature at which a liquid will evolve sufficient vapors to form a flammable mixture with air under equilibrium conditions.[5] This temperature is applicable for assessing flammability in large process vessels and similar equipment.

Two examples of open cup methods are the ASTM D92[6] and ASTM 1310[3]. The ASTM D 92 method is primarily used for viscous material having a T_f of 79 °C and above.

2.2   FLASH POINT THEORETICAL METHODS

Several methods have been developed for the prediction or estimation of the flash points of pure compounds and mixtures. A review of most of these methods has been published in the journal of *Process Safety Progress.*[17] However, in this section only the most relevant estimation methods according to the best judgment of the author will be presented.

2.2.1   Pure compounds

The flash point values of pure organic compounds can be estimated from the correlation of the flash point as a function of the boiling point developed by Satyanarayana and Rao.[18] The correlation is presented below:

$$T_f = a + \frac{b \left(\dfrac{c}{T_b} \right)^2 e^{\frac{-c}{T_b}}}{\left(1 - e^{\frac{-c}{T_b}} \right)^2} \qquad (1)$$

where,

T_f is the flash point temperature (K),
a, b, and c are constants provided in the original source[18], and
T_b is the boiling point temperature of the material (K).

The equation was fit for over 1,200 compounds with less than 1% absolute error with experimental data (based on K). Larger deviations, of approximately 10 °C, were found for the phosphorous chemical group. A comparison of this and other correlations are presented in the original paper.[18]

Flash points of pure compounds can also be obtained from Quantitative Structure Property Relationships (QSPR), which are correlations that relate a flash point value with molecular descriptors.   The QSPR approach finds quantitative mathematical relationships between the intrinsic molecular structure and observable properties of chemical compounds. Katritzky *et al.*[19] used QSPR to develop the following three-parameter correlation for the flash point:

$$T_F = (44.50 \pm 0.99)^3 \sqrt[3]{G_b} + (16731 \pm 574.45)HDCA + \\ (4.95 \pm 0.73)M_R - (117.70 \pm 9.14) \qquad (2)$$

where,

$\sqrt[3]{G_b}$ is the cubic root of the gravitational index,
HDCA is a hydrogen donor charged solvent accessible surface area, and
M_R is the molecular weight divided by the number of atoms in the molecule.

The molecular descriptors can be obtained by using a quantum chemical package that includes drawing and optimizing the molecule. A review of molecular descriptors is given by Karelson.[20]

2.2.2   Binary mixtures

Mathematically, the flash point is the temperature at which the vapor pressure is equivalent to the LFL composition.

$$LFL_i = \frac{P_{i,fp}{}^{sat}\left(T_f\right)}{P} \tag{3}$$

where $P_{i,fp}{}^{sat}$ (T_f) is the vapor pressure at the flash point temperature and P is the ambient pressure. Equation (3) shows the relationship between the flammability properties LFL and T_f. The first one is a vapor phase property, while the other is a liquid phase property. Thermodynamically, the relation between an ideal vapor and a non-ideal liquid is represented by the equilibrium condition presented in Equation (4).

$$y_i P = x_i \gamma_i P_i{}^{sat} \qquad or \qquad y_i = \frac{x_i \gamma_i P_i{}^{sat}}{P} \tag{4}$$

where x_i, y_i, γ_i, and $P_i{}^{sat}$ are the liquid mole fraction, vapor mole fraction, activity coefficient of component i in the liquid, and vapor pressure at temperature T, respectively.

The Le Chatelier rule for the flammable vapor-air mixture of two components is:

$$\frac{y_1}{LFL_1} + \frac{y_2}{LFL_2} = 1 \tag{5}$$

where y_1 and y_2 refer to the vapor mole fraction of components 1 and 2, and LFL_1 and LFL_2 refer to the lower flammable limit of component 1 and 2. Details on the derivation of Equation (5) are given by Mashuga and Crowl.[21] The assumptions made in the derivation of the rule were found to be reasonably valid at the LFL, which is closely related to the T_f.

The flash point of a binary mixture can be estimated by the model developed by Liaw, *et al.*[22]

$$\frac{x_1 \gamma_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \tag{6}$$

where x_i, γ_i, P_i^{sat}, and $P_{i,fp}^{sat}$ are the liquid mole fraction, liquid phase activity coefficient, vapor pressure at temperature T and vapor pressure at T_f of the ith mixture component, respectively. This model is a result of the combination of Equations (3), (4) and (5).

Other prediction models are presented in the literature for the prediction of mixture flash point. More information on these models can be found in the literature.[23-29] However, Liaw model[22] presented in Equation (6), is the model selected in this work for the prediction of mixture flash point.

2.2.2.1 Aqueous mixtures

An aqueous mixture contains water and a flammable component. In industry these mixtures are known as waste solutions in which for example there is a large amount of water with a small amount of a solvent. Water is a nonflammable component, and therefore has no T_f. The lowest T_f that these mixtures can exhibit is the T_f of the flammable component.

Usually water is used as a diluent because it does not contribute to the flammability properties of the flammable component. The effectiveness of water as a hazard control, by increasing the T_f of the mixture, can be studied with a prediction model that considers flammable and non flammable components. The prediction model for aqueous solutions is a reduced version of the original Liaw model (Equation 6):

$$\frac{x_1 \gamma_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \qquad (7)$$

In this model, water is assumed to be component 1 and the flammable compound is component 2. More information on this model is given by Liaw and Chiu.[30] The temperature that satisfies Equation (7) is the flash point temperature of the mixture.

2.2.2.2 Flammable mixtures

Flammable mixtures are composed of two flammable compounds. Three different behaviors can be expected depending on whether the mixture is ideal or non-ideal. If the mixture is non-ideal with positive deviations from Raoult's law, more molecules than for ideal behavior will escape to the vapor phase which raises the vapor pressure of the mixture. Since in this case both chemicals are flammable, a higher vapor pressure results in a lower flash point value to reach the LFL. Another behavior is expected when the mixture is non-ideal with negative deviations from Raoult's law, where the mixture vapor pressure is lower than the vapor pressure of the individual components.

Therefore, mixture flash point values are expected to be higher than the pure component flash points. However, this behavior was not confirmed in this work because these mixtures are rare. Liaw model[22], presented in Equation (6), is the recommended prediction model when uncertainties exist regarding the ideality of the mixture.

In an ideal mixture, all A-A, B-Band A-B interactions are equal. In other words, there is no preference between the interactions of like or unlike molecules. These mixtures follow Raoult's law, in which the equilibrium condition between the vapor and liquid phase is represented by:

$$y_i P = x_i P_i^{sat} \qquad or \qquad y_i = \frac{x_i P_i^{sat}}{P} \qquad (8)$$

where x_i, y_i, and P_i^{sat} are the liquid mole fraction, vapor mole fraction, and vapor pressure of component i at temperature T, respectively. The combination of Equations (3), (5) and (8) is the basis for the flash point prediction model of ideal mixtures, which is presented in Equation (9).

$$\frac{x_1 P_1^{sat}}{P_{1, fp}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2, fp}^{sat}} = 1 \qquad (9)$$

2.3 MINIMUM FLASH POINT BEHAVIOR (MFPB)

MFPB is for a mixture flash point that is less than either of the values of the corresponding individual mixture components.[15]   The liquid solution with MFPB is likely to be more hazardous than the individual components of the solution, because the flash point of the solution over a range of compositions is lower than the recorded flash points for the individual solution components.[22]

This behavior is attributable to non-ideal mixtures exhibiting positive deviations from Raoult's law. In mixtures showing a positive deviation from Raoult's law, the vapor pressure of the mixture is higher than expected from an ideal mixture. If both components are flammable, the temperature needed to achieve the mixture LFL is lower. Mixtures with highly positive deviations from Raoult's law can exhibit MFPB. This concept is illustrated qualitatively in Figure 3.
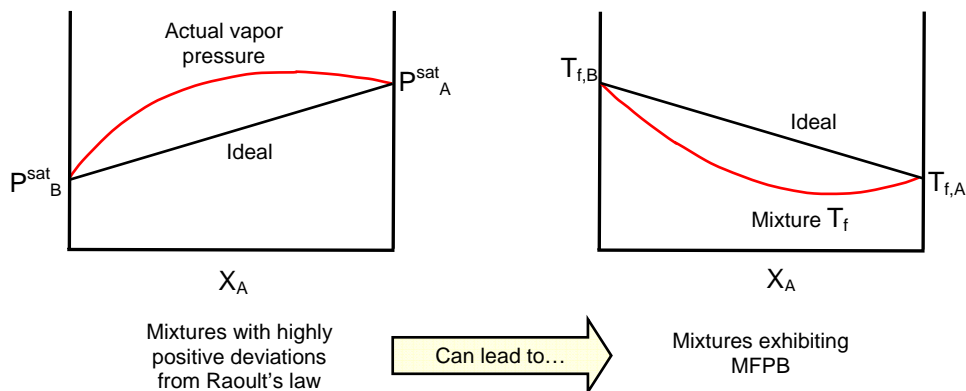
Figure 3. Qualitative representation of the relation between mixture vapor pressure and mixture flash point.

The mixture flash point will not have a shape exactly opposite to the mixture vapor pressure shape. Figure 3 is just intended to show that highly positive non-ideal mixtures can result in mixtures with MFPB.

The earliest data about MFPB published in the literature, to the best knowledge of the author, is from 1976 by the work done by Chevron Research Company.[31] This work is focused on solvent flash points, and it was found that dissimilar molecular species form non-ideal blends that usually have lower flash points than might be expected. Later in 1984, Anderson and Magyari[32] reported that the flash points of methanol-hydrocarbon solutions are frequently lower than the flash points of either constituent.

In 1998, Larson[33] studied five binary systems known to exhibit minimum boiling point azeotropic behavior. Flash point depression was confirmed in three of the five systems studied. The study was done experimentally and theoretically using the Wilson and modified regular solution theory for the estimation of activity coefficient. This latter model is not suitable for aqueous mixtures.

In 2002, Liaw[22] published his model for the prediction of the flash point of binary mixtures. In the theoretical work Liaw used G^{ex} models that depend on the availability of experimental data (see Section 2.4.1) for the binary interaction parameters due to their simplicity compared to purely theoretical models. He also developed sufficient conditions[15] for a binary liquid solution to behave as a MFPB solution.

2.4   CLASSIFICATION OF MIXTURES

Mixtures are classified as ideal or non-ideal mixtures. An ideal solution has an $\gamma_i =$ 1. These solutions result from mixing two similar materials and no differential energies of interaction are encountered between the components. However, most solutions are not ideal.

Non-ideal solutions have an activity coefficient value smaller or greater than 1. Negative deviation solutions from Raoult's law are characterized by strong attractive forces between mixture components, molecules prefer to be in solution, and $\gamma_i < 1$. Positive deviation solutions from Raoult's law have strong repulsive forces between mixture components, molecules prefer to be in the gas phase, and $\gamma_i > 1$.

2.4.1   Activity coefficient models

The activity coefficient, γ_i, is a dimensionless parameter that measures the deviation from ideality in a mixture. Some of the G^{ex} energy function models that can be used to obtain the activity coefficients are: NRTL, Wilson, UNIQUAC, and UNIFAC. Each of these models is presented in Table 2.

The first three G^{ex} models presented in Table 2 to calculate the activity coefficients depend on experimental interaction parameters. Wilson contains only two adjustable parameters unlike NRTL and is mathematically easier than UNIQUAC. The Wilson and NRTL models require only binary mixture information to obtain values of the parameters, whereas the UNIQUAC model also requires pure component molar volumes as well as surface area and volume parameters.[34]

The NRTL model is best fitted for aqueous organic mixtures while the Wilson is for alcohols, phenols, and aliphatic hydrocarbons. The UNIQUAC is best fitted for hydrocarbons, ketones, esters, water, amines, alcohols, nitriles, etc.[34]

Table 2. Some Activity Coefficient (G^{ex} Energy) Models

Model	Binary Parameters	ln γ$_1$ and ln γ$_2$
NRTL	$g_{12} - g_{22}, g_{21} - g_{11}$	$\ln \gamma_i = x_j^2 \left[\tau_{ji} \left(\dfrac{G_{ji}}{x_i + x_j G_{ji}} \right)^2 + \dfrac{\tau_{ij} G_{ij}}{\left(x_j + x_i G_{ij} \right)^2} \right]$ where $i = 1\, j = 2 \text{ or } i = 2\, j = 1$ $\tau_{ij} = \dfrac{g_{ij} - g_{jj}}{RT}; \ln G_{ij} = -\alpha_{ij} \tau_{ij}$
Wilson	$\Lambda_{12}, \Lambda_{21}$	$\ln \gamma_i = -\ln\left(x_i + \Lambda_{ij} x_j \right) + x_j \left(\dfrac{\Lambda_{ij}}{x_i + \Lambda_{ij} x_j} - \dfrac{\Lambda_{ji}}{\Lambda_{ji} x_i + x_j} \right)$ where $i = 1\, j = 2 \text{ or } i = 2\, j = 1$ $\Lambda_{ij} = \dfrac{v_j^l}{v_i^l} \exp\left(-\dfrac{\lambda_{ij} - \lambda_{ii}}{RT} \right)$
UNIQUAC	$u_{12} - u_{22}, u_{21} - u_{11}$	$\ln \gamma_i = \ln \dfrac{\Phi_i}{x_i} + \dfrac{z}{2} q_i \ln \dfrac{\theta_i}{\Phi_i} + \Phi_j \left(l_i - \dfrac{r_i}{r_j} l_j \right) - q_i \ln\left(\theta_i + \theta_j \tau_{ji} \right)$ $+ \theta_j q_i \left(\dfrac{\tau_{ji}}{\theta_i + \theta_j \tau_{ji}} - \dfrac{\tau_{ij}}{\theta_j + \theta_i \tau_{ij}} \right)$ where $i = 1\, j = 2 \text{ or } i = 2\, j = 1$ $\ln \tau_{ij} = -\dfrac{u_{ij} - u_{jj}}{RT}; \Phi_i = \dfrac{x_i r_i}{x_i r_i + x_j r_j}; \theta_i = \dfrac{x_i q_i}{x_i q_i + x_j q_j}; l_i = \dfrac{z}{2}\left(r_i - q_i \right) - \left(r_i - 1 \right)$ $z = 10$

Table 2. Continued

Model	Binary Parameters	$\ln \gamma_1$ and $\ln \gamma_2$
UNIFAC	Group interaction parameters, a_{mn} and a_{mn}	

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R$$

$$\ln \gamma_i^c = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\left(x_i l_i + x_j l_j\right)$$

$$\Phi_i = \frac{x_i r_i}{x_i r_i + x_j r_j}; \theta_i = \frac{x_i q_i}{x_i q_i + x_j q_j}; l_i = \frac{z}{2}\left(r_i - q_i\right) - \left(r_i - 1\right), r_i = \sum_k v_k^{(i)} R_k; q_i = \sum_k v_k^{(i)} Q_k$$

$$\ln \gamma_i^R = \sum_k v_k^{(i)}\left(\ln \Gamma_k - \ln \Gamma_k^{(i)}\right)$$

all groups

$$\ln \Gamma_k = Q_k\left[-\ln\left(\sum_m \theta_m \Psi_{mk}\right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}}\right]$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}; \Psi_{mn} = \exp\left(-\frac{U_{mn} - U_{nn}}{RT}\right) = \exp\left(-\frac{a_{mn}}{T}\right)$$

θ_m = surface area fraction of group m; Φ_i = segment fraction; X_m = mole fraction of group m in the mixture; $v_k^{(i)}$ = number of k groups present in species i; $\ln \Gamma_k^{(i)}$ = residual contribution to the activity coefficient of group k in a pure fluid of species i molecules; R_k = group volume parameter; Q_k = surface area parameter

More information about these models can be obtained from Orbey and Sandler,[34] and Poling and Prausnitz.[35]

What can be done in the absence of experimental data from which to obtain the model parameters? In this case it is necessary to make complete predictions, and UNIFAC is the only one from the models in Table 2 that does not require experimental binary interaction parameters. The contributions due to molecular interactions, parameters a_{mn} and a_{nm}, are obtained from a database using a wide range of experimental results. Some of these parameters are given by Poling *et al.*[35] The advantage of the UNIFAC method is that mixtures composed of the same functional groups can be studied using the same binary parameters.

The UNIFAC model is the group contribution version of the UNIQUAC model. In this model each molecule is considered to be a collection of functional groups and the behavior of a mixture can be predicted based on known functional group-functional group interactions (or interaction parameters).[34] When using UNIFAC model the functional subgroups must be identified in each molecule.

2.4.2   Infinite dilution activity coefficients and Quantum Chemistry

The activity coefficient at infinite dilution, γ^{∞}, is a useful measure of the degree of non-ideality in a liquid mixture. Such data may also be used to regress binary interaction parameters for the NRTL, Wilson, and UNIQUAC activity coefficient models.[36] The model most often employed for predictive purposes is the UNIFAC model.

COSMO-RS (COnductor-like Screening MOdel for Real Solvents) is an alternative predictive tool for thermodynamic properties of liquids and mixtures based on quantum chemical calculations. It is a theory that describes the interactions in a fluid as local contact interactions of molecular surfaces, and the interaction energies are quantified by values of screening charge densities σ and σ' that form a molecular contact.[37] These screening charge densities can be described as molecular descriptors and provide information about the polarity of the molecules. The σ-profile of various compounds is presented in Figure 4.
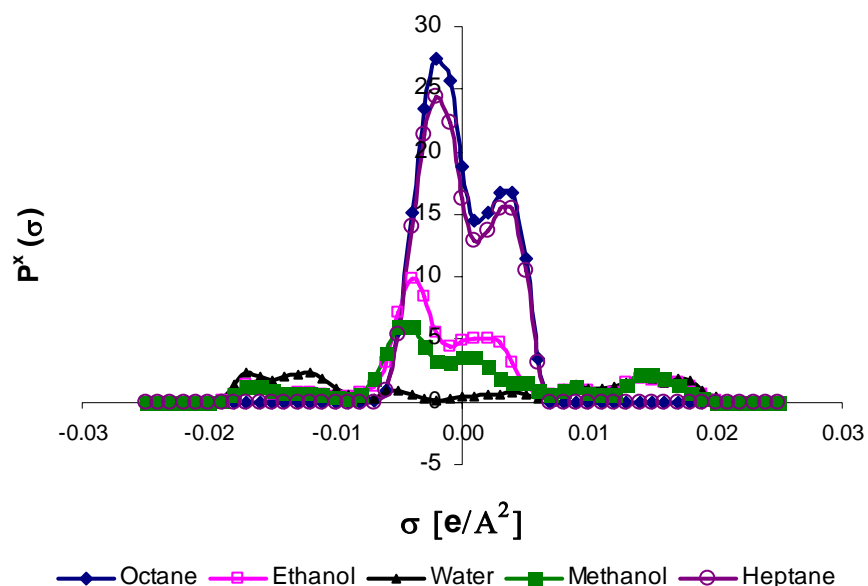
Figure 4. Screening charge profiles for various compounds obtained using COSMO-RS.

In the UNIFAC model the mixture is considered as a collection of functional groups, and the binary interaction parameters depend on these functional groups. In COSMO-RS, the interactions between the liquid molecules are described by the screening charge densities at the local contact area. The advantage of COSMO-RS is that it can be used in the task of screening a large number of compounds from a database.[36]

In this work, COSMO-RS was used to obtain γ^{∞} which were used with the rules developed by Liaw[15] to identify which mixtures will exhibit MFPB. More information on this procedure is presented in Chapter 3.

In general COSMO-RS tends to have larger percent absolute deviations for the predictions of γ^{∞} when compared with UNIFAC models. Good systems for COSMO-

RS include alkanes in alcohols, alkyl in alkanes, ketones in alkanes, and alkanes in alkyl halides. [36]

CHAPTER III

PROCEDURE FOR THE EVALUATION OF MIXTURE FLASH POINTS

This chapter discusses the hierarchical process that should be followed when evaluating the flash point of a binary mixture. If experimental data are available for the mixture, the evaluation process is finished. However, if no experimental data are available at that point, estimation methods, correlations, and some assumptions can be valid depending on the mixture. There are certain guidelines that can be followed to decide when assumptions are appropriate and when more experimental data are needed.

A screening procedure based on Liaw's rules[15] that allow for the evaluation of mixtures exhibiting MFPB is also discussed. The advantage of this procedure is that more time and effort can be spent on those mixtures identified as MFPB mixtures.

The required input data to estimate the mixture flash point are discussed as well as different techniques and resources that can be used to estimate parameters and obtain input data. The most difficult data needed are the binary interaction parameters for the activity coefficient models. Different alternatives are presented to obtain them in the procedure for the evaluation of mixture flash point.

3.1 PURPOSE

The procedure presented here for the estimation of binary mixture flash point is a tool that highlights the basic input information needed to determine mixture flash point. For each parameter needed, different estimation methods or correlations are provided, which the user will select according to the specific needs and based on the characteristics of the mixture. A flowchart that depicts the critical questions that should be answered to decide whether certain assumptions can be accepted, more detailed estimations methods are needed, or more experimental data are necessary is presented in Figure 5.
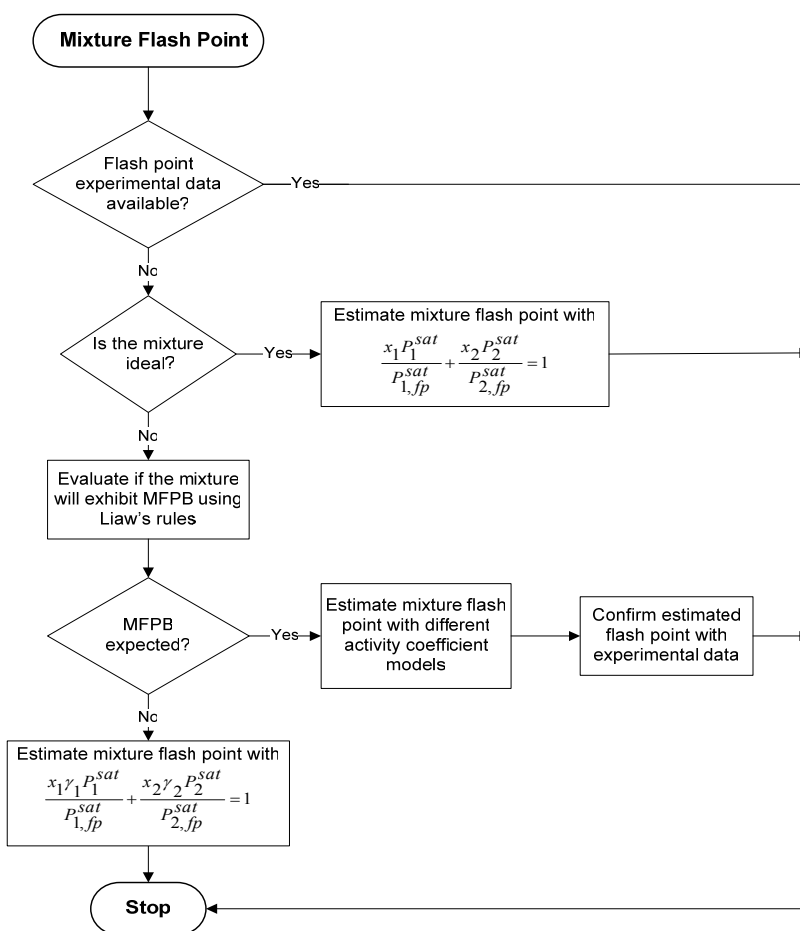
Figure 5. Flowchart that describes the steps for the determination of mixture flash points.

3.2 INITIAL PHASE: SCREENING METHODOLOGY

To identify a binary mixture exhibiting MFPB, Liaw *et al.*[15] developed necessary conditions, which are presented in Figure 6. The mixture component with the lowest flash point value is designated as component #1 to apply these conditions.

Set $T_{fp1} < T_{fp2}$
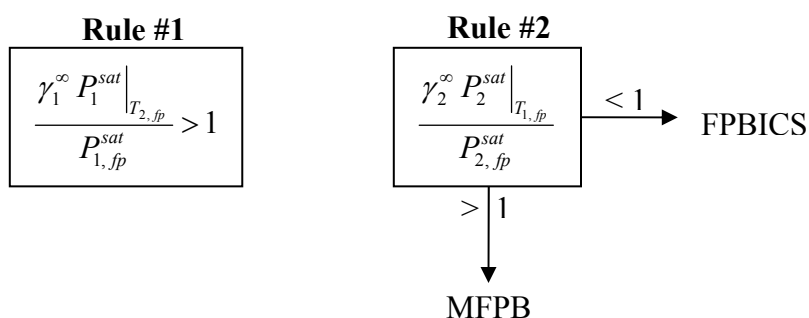
Figure 6. Conditions to identify a mixture that exhibits MFPB as developed by Liaw *et al.*[15] (MFPB: Minimum flash point behavior, FPBICS: Flash point between individual components)

The rules are based on the estimation of the vapor pressures of each mixture component at its own flash point temperature and at the flash point temperature of the other component.   The activity coefficients at infinite dilution are also needed $\left(\gamma_i^\infty = \gamma_i \big|_{x_i \to 0} \right)$, which can be estimated by using any of the G^{ex} models presented in Table 2 of Chapter II or COSMO-RS.

The general theoretical method COSMO-RS was used to estimate the γ_i^∞, which were then used in the rules presented in Figure 6 to analyze its usefulness for the identification of mixtures exhibiting MFPB. The COSMO-RS calculations were performed using $C^2 \cdot DMol^3$ with the input data presented in Table 3.

Table 3. Input Data Used for COSMO-RS Calculations

Chemical	Antoine coefficients			Gas phase energy [Ha]
	A	B	C	
Octane	6.90940	1349.820	209.385	-315.7187610
Heptane	6.89385	1264.370	216.636	-276.4041106
Ethanol	8.21330	1652.050	231.480	-155.0456301
1-Butanol	7.47680	1362.390	178.730	-233.6744593

The Antoine coefficients were obtained from the database of the University of Maryland,[38] and the gas phase energies were calculated using Gaussian 03[39]. The gas phase energies were obtained using the b3lyp level of theory and the 6-31+g(d) basis set. The flash point for the individual components were obtained from NFPA 325[12]. The results obtained for 3 mixtures are presented in Table 4.

Table 4. Results Using COSMO-RS to Obtain γ^∞ to Identify Mixtures Exhibiting MFPB

Mixture	Rule #1	Rule #2	Classification
	$\dfrac{\gamma_1^\infty \left. P_1^{sat}\right|_{T_{2,fp}}}{P_{1,fp}^{sat}} > 1$	$\dfrac{\gamma_2^\infty \left. P_2^{sat}\right|_{T_{1,fp}}}{P_{2,fp}^{sat}}$	
Heptane (1) – Octane (2)	2.7555	0.3145	FPBICS
Octane (1) – 1-Butanol (2)	15.5909	16.3828	MFPB
Octane (1) – Ethanol (2)	9.5680	294.4660	MFPB

When compared with the original source[15], where the activity coefficients were calculated using a G^{ex} model, the results obtained with COSMO-RS are lower for Rule #1 and higher for Rule #2. However, the results comply with the inequality in Rule #1 (>1) and they predict correctly the mixtures that exhibit MFPB. It is important to note that uncertainties in the parameters used for the vapor pressures cancel out in both rules. Then, a successful identification of a mixture with MFPB depends on the γ_i^{∞} values.

If the results obtained for the γ_i^{∞} with COSMO-RS are not accurate, the results in the classification when applying the rules may be the prediction of a mixture with MFPB when in fact it is a mixture with FPBICS. This prediction will not present any hazard, since it will assume that the flash point for the mixture could be lower than the flash point of the individual components. On the contrary, if the prediction were the opposite, the results obtained with COSMO-RS would result in a hazardous misclassification.

The advantage of using COSMO-RS is that the screening charge that is used as an input in the calculations must be calculated just once per chemical, so the user can create a database of different chemicals and then apply the rules for different mixtures to screen the ones that have the potential of exhibiting MFPB.

3.3 ESTIMATION OF BINARY MIXTURE FLASH POINT

The basic information needed for the estimation of a binary mixture flash point is:

- flash points of the individual components of the mixture,
- vapor pressure of each mixture component, and
- activity coefficient of each component.

When vapor-liquid experimental data are available for the mixture of interest, the flash point calculation is straightforward by applying the model developed by Liaw *et al.* [22, 30] and presented in Equation (6). However, sufficient data are often unavailable, and other ways of obtaining the basic information are needed.

A procedure to estimate the flash point of binary mixtures was developed and is presented in Figure 7. This procedure is based on obtaining the data needed for the model of Liaw *et al.*[22] and it includes the option of determining some of the basic parameters from quantum chemical calculations or from correlations.

3.3.1 Flash point

The experimental flash point values for the individual components of the mixture can be obtained by any of the standard test methods discussed in Chapter II. From the two experimental test methods, the closed cup methods are preferred over the open cup methods. The flash point estimation methods for pure compounds were discussed in section 2.2.1 of Chapter II.
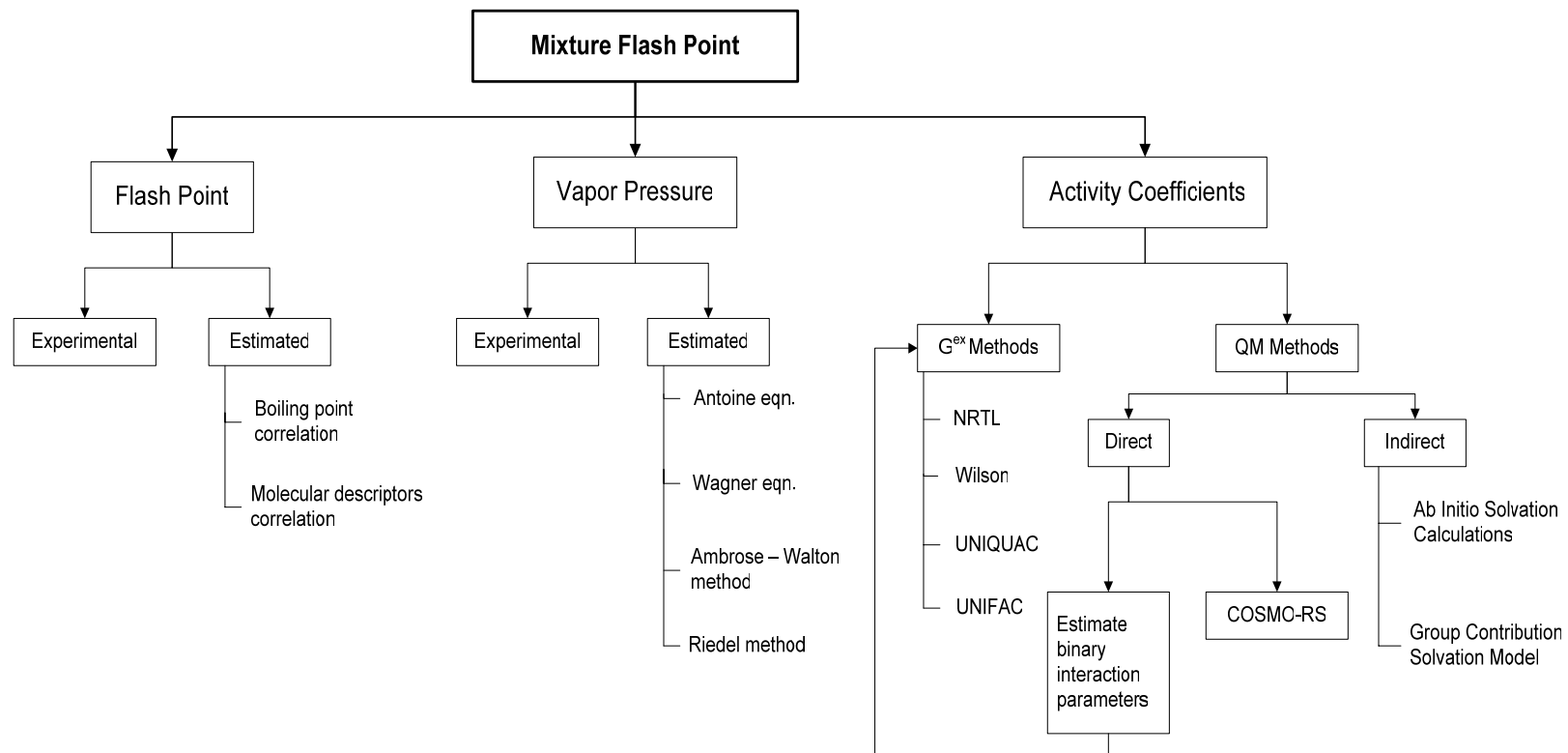
Figure 7. Procedure to estimate the flash point of binary mixtures.

3.3.2   Vapor pressure

An equation for the saturated vapor pressure, P_i^{sat}, of each mixture component as a function of temperature is needed to estimate the mixture flash point. One of the most common correlations is the Antoine equation:

$$\log P_i^{sat} = A_i - \frac{B_i}{T + C_i} \tag{10}$$

where A_i, B_i and C_i are the parameters of compound i. This correlation should not be used outside the temperature range at which the parameters were obtained. Usually in the range of 0.01 to 2 bar, the Antoine equation provides excellent results. The parameters for the Antoine equation can be obtained from collections such as Boublik *et al.*[40] and Poling *et al.*[41], or from online databases such as the NIST Chemistry WebBook[42].

Another alternative to obtain vapor pressure data is the extended Antoine equation. This correlation is presented in (11)

$$\log P_i^{sat} = A_i + \frac{B_i}{T} + C_i \log T + D_i T + E_i T^2 \tag{11}$$

where P is in mmHg and T is in K. A_i, B_i, C_i, D_i and E_i are the regression coefficients for compound i. Usually the valid temperature range of this correlation is wider than correlation (10). The Chemical Properties Handbook[43] contains extended Antoine equation regression coefficients for 1,355 organic compounds and 343 inorganic compounds.

Another correlation that can be used for the estimation of vapor pressure is the Wagner equation presented in (12):

$$\ln P_i^{sat} = \frac{a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6}{T_r} \qquad (12)$$

where $\tau = 1 - T_r$, and T_r corresponds to the reduced temperature, which is defined by $T_r \equiv T/T_c$, where T_c is the critical temperature. This correlation is one of the most accurate ones, because it is constrained to generate a "reasonable shape" for the vapor pressure curve from a reduced temperature of 0.5 up to the critical point.[41] The parameters for this correlation can be found in *The Properties of Gases and Liquids*[35].

If no experimental data are available, the vapor pressures can be estimated by the Ambrose-Walton and/or Riedel methods. Properties needed for these two methods are the critical temperature (T_c), critical pressure (P_c), and boiling point temperature (T_b) for Vetere's modification of the Riedel method, and the acentric factor (ω), T_c, and P_c for the Ambrose-Walton method. Equations for both methods can be found in Poling *et al.*[35]

3.3.3 Activity coefficients

The activity coefficients can be obtained from any of the G^{ex} models presented in Table 2 of Chapter II. Another alternative is to use Quantum Mechanics (QM) calculations. The use of QM calculations is divided into two methods: direct and indirect. In the direct methods the activity coefficients are calculated directly by employing the QM calculations. In the indirect methods, the activity coefficients at infinite dilution are obtained from solvation energies.

In the direct methods, binary interaction parameters are obtained theoretically. Then, these parameters are employed in any of the G^{ex} models to obtain the activity coefficients. Sum and Sandler[44] proposed an approach based on a combination of ab initio quantum mechanical (QM) methods and the activity coefficient model. This approach for the prediction of vapor liquid equilibria (VLE) for a number of hydrogen

bonded binary mixtures is based on the construction of a molecular cluster model, which was normally made of eight molecules. However, the cluster size depends on the sizes of the molecules that compose the mixture. In other words, the critical cluster size must be addressed for each mixture. An assumption that is made when applying this methodology to estimate the activity coefficients is that the binary interaction parameters are not temperature dependent.

Neiman, *et al.*[45] employed the same methodology, but instead of using quantum mechanical methods, they employed molecular dynamics (MD) simulations to evaluate molecular interactions in the liquid. They claim that MD simulations can describe very well the behavior of liquids if a sufficiently large unit cell is used. In this case, the calculations are dependent upon the size of the unit cell, the simulation time, and the method used to evaluate the interaction energies.

COSMO-RS is classified as a direct method because it allows for the estimation of activity coefficients at infinite dilution directly. The input data needed to employ this method are the Antoine coefficients and the gas phase energies, which can be obtained with Gaussian[39] or any other QM software.

A Group Contribution Solvation (GCS) model was developed by Lin and Sandler[46] to calculate infinite dilution activity coefficients based on computational chemistry. The electrostatic part of the free energy is obtained from various continuum solvation models, and the two energy parameters in the UNIQUAC model are related to the attractive part of the solvation free energy. The fundamental equation that allows the calculation of γ_i^∞ from solvation energies is presented in (13).

$$RT \ln \gamma_i^\infty = \Delta G_{i/j}^{*sol} - \Delta G_{i/i}^{*sol} + RT \ln \frac{\rho_2^0}{\rho_1^0} \tag{13}$$

where

$\Delta G_{i/j}^{*sol}$ is the free energy change of the solvation of solute i in solvent j,

$\Delta G_{i/i}^{*sol}$ is the free energy change of the solvation of solute i in solvent i, and

ρ_i^0 is the density of liquid i.

According to Lin and Sandler[46], the GSC model yields results with lower average errors for the γ_i^∞ of water, n-hexane, acetonitrile, and n-octanol when compared with UNIFAC and the modified UNIFAC model. In the modified UNIFAC the combinatorial part was changed for representing compounds very different in size. Also temperature dependent parameters were introduced. More information can be found in Gmehling and Schiller[47]. In conclusion, the GSC models seem to be more precise in the calculation of γ_i^∞, but are more difficult and time consuming to apply due to the QM knowledge required. However, it is an estimation alternative for new compounds.

More information about GSC models to predict γ_i^∞ can be found in the work of Nanu and Loos[48]. They used this approach to obtain the γ_i^∞ of aroma compounds in water. Aroma compounds are usually higher alcohols, and their derived acetyl esters are important flavor components.

CHAPTER IV

PREDICTION OF BINARY MIXTURE FLASH POINT

This chapter includes the flash point prediction of binary mixtures. The mixtures are classified as flammable or aqueous, for which one of the components is water.

All of the predictions are done assuming ideal vapors above ideal and non-ideal liquid solutions. For that, equations (6) and (9) of Chapter II are employed. The purpose of showing both predictions on one graph is to dramatize the erroneous prediction that could be made if an ideal solution is assumed when the solution is non-ideal. The flash point of the individual components are obtained from NFPA 325[12], which is based on closed cup tests, unless otherwise specified. The vapor pressure as a function of T of each mixture component is obtained from the extended Antoine equation (see equation (11) in Chapter III). Most of the parameters needed for the extended Antoine equation are from the *Chemical Properties Handbook*[43] and are presented in Appendix A.

Flash point predictions assuming non-ideal behavior using different G^{ex} models were performed by iterative calculations in Excel. A generic file for the calculation of binary mixture flash point using NRTL, Wilson, and UNIQUAC is included with this work. Instructions on how to use each of these files are provided in Appendix B. A generic file for the calculation of binary mixture flash point using UNIFAC is not provided because the functional groups that compose the mixture must be identified first, and the number of interaction parameters will depend on these functional groups. Appendix C contains the UNIFAC functional groups used in this work for the chemicals of the mixtures studied.

4.1 AQUEOUS MIXTURES

Aqueous mixtures here are binary mixtures with water as one of the components and a flammable component. Background information on these mixtures is provided in section 2.2.2.1 of Chapter II.

4.1.1   Water – Methanol

The flash point of pure methanol is 11 °C according to NFPA 325[12]. However, the experimental flash point of methanol obtained by Liaw *et al.*[30] is 10 °C, which is the flash point value selected in this work for all predictions. The parameters used in each G^{ex} model for the calculation of activity coefficients needed for the flash point predictions are presented in Table 5.

Table 5. Parameters Used in the G^{ex} Models for the Flash Point Prediction of the Water - Methanol Mixture

G^{ex} model	Parameters		Reference
	A_{12}	A_{21}	
Wilson	908.46	-359.74	49
UNIQUAC (A)	-271.26	736.01	49
UNIQUAC (B)	180.22	-117.34	50
UNIQUAC (QM)	6.37	-47.51	44

Wilson equation: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$; UNIQUAC equation: $A_{12} = (u_{12} - u_{22})/R$, $A_{21} = (u_{21} - u_{11})/R$

The predictions for the water – methanol mixture flash point are presented in Figure 8. Experimental binary interaction parameters (BIP's) as well as parameters obtained from QM calculations were used in the predictions with the UNIQUAC model. Better results are obtained from experimental BIP's, but reasonably results are obtained with QM BIP's.
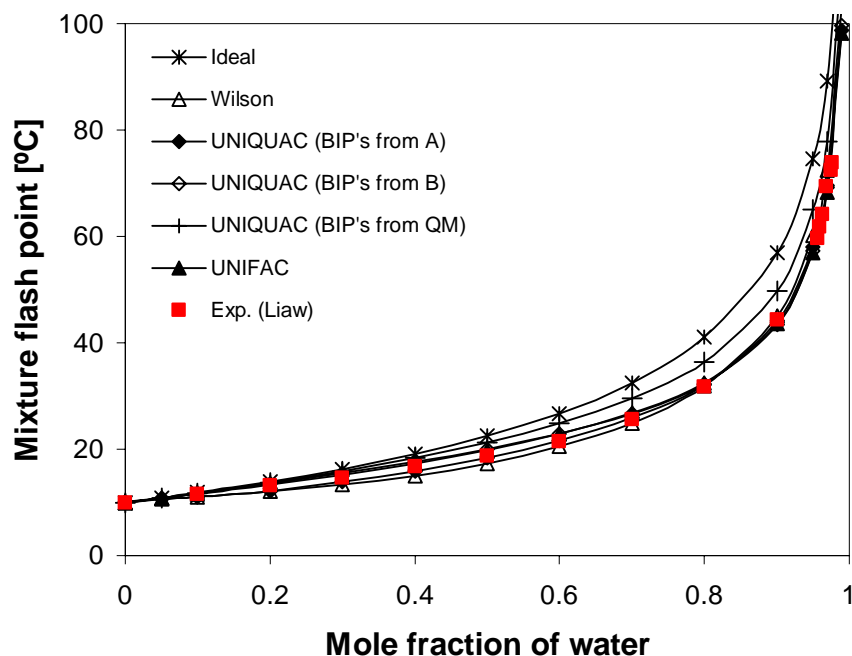
Figure 8. Prediction of the water - methanol mixture flash point.

All the predictions agree with the experimental data obtained from Liaw *et al*.[30] The trend of the experimental mixture flash point is predicted accurately with all of the parameters analyzed. Even UNIFAC, which is based on theoretical parameters, agree with the experimental data. Larger deviations between the ideal predicted values and experimental data are obtained as the water content is increased. At a water mole fraction of 0.9, the difference in the T_f from ideal behavior and experimental data is approximately 12 °C.

4.1.2 Water - Ethanol

The flash point of pure ethanol is 13 °C according to NFPA 325[12]. The parameters used in each G^{ex} model for the calculation of activity coefficients needed for the flash point predictions are presented in Table 6.

Table 6. Parameters Used in the G^{ex} Models for the Flash Point Prediction of the Water - Ethanol Mixture

G^{ex} model	Parameters			Reference
	A_{12}	A_{21}	α_{12}	
NRTL	633.91	24.86	0.4	51
Wilson	481.44	179.66	-	52
UNIQUAC	-109.37	299.46	-	52
UNIQUAC (QM)	131.57	-4.49	-	44

NRTL equation: $A_{12} = (g_{12} - g_{22})/R$, $A_{21} = (g_{21} - g_{11})/R$; Wilson equation: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$; UNIQUAC equation: $A_{12} = (u_{12} - u_{22})/R$, $A_{21} = (u_{21} - u_{11})/R$

The predictions for the water – ethanol mixture flash point are presented in Figure 9. Experimental binary interaction parameters (BIP's) as well as parameters obtained from QM calculations were used in the predictions with the UNIQUAC model. Mixture flash point predictions obtained with the UNIQUAC model, using BIP's either from experimental data or from QM calculations, agree with the experimental data.

All G^{ex} models predict satisfactorily the trend of the experimental flash point data. The ideal solution model predicts higher flash point values of approximately 20 °C around the water mole fraction of $x_1 = 0.9$.

Figure 9. Prediction of the water - ethanol mixture flash point.

4.1.3 Water – 1-Propanol

The flash point of pure 1-propanol is 23 °C according to NFPA 325[12]. However, the experimental flash point of 1-propanol obtained by Liaw *et al.*[30] is 21.5 °C, which is the flash point value selected in this work for all predictions. The parameters used in each G^{ex} model for the calculation of activity coefficients needed for the flash point predictions are presented in Table 7.

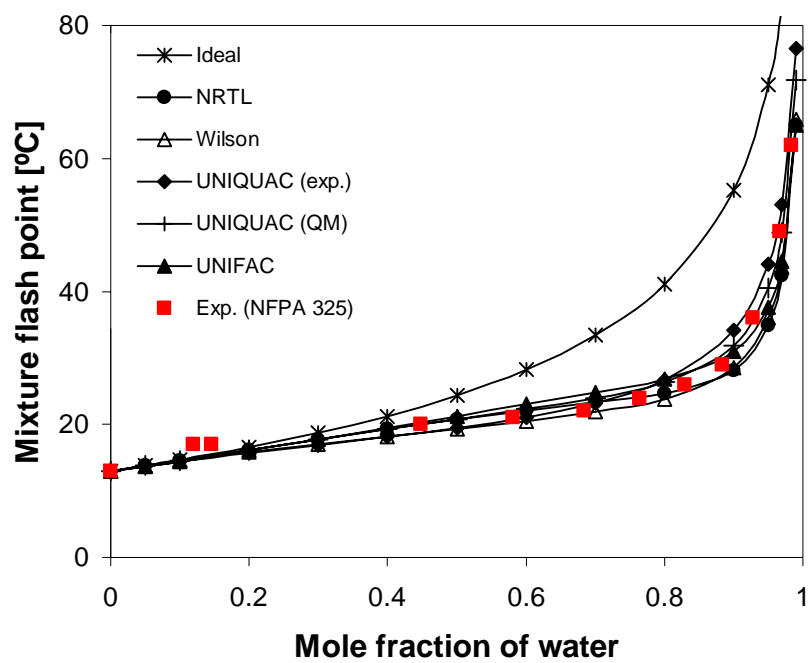**Table 7. Parameters Used in the G^{ex} Models for the Flash Point Prediction of the Water - 1-Propanol Mixture**

G^{ex} model	Parameters			Reference
	A_{12}	A_{21}	α_{12}	
NRTL	865.41	77.33	0.377	53
Wilson	597.52	527.50	-	54
UNIQUAC	200.64	9.58	-	55
UNIQUAC (QM)	146.19	77.85	-	44

NRTL equation: $A_{12} = (g_{12} - g_{22})/R$, $A_{21} = (g_{21} - g_{11})/R$; Wilson equation: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$; UNIQUAC equation: $A_{12} = (u_{12} - u_{22})/R$, $A_{21} = (u_{21} - u_{11})/R$

The predictions for the water – 1-propanol mixture flash point are presented in Figure 10. Experimental binary interaction parameters (BIP's) as well as parameters obtained from QM calculations were used in the predictions with the UNIQUAC model. Mixture flash point predictions obtained with the UNIQUAC model, using BIP's either from experimental data or from QM calculations, agree with the flash point experimental data.

All G^{ex} models predict satisfactorily the trend of the experimental flash point data. The ideal solution model predicts higher flash point values for any water mole fraction equal or higher than $x_1 = 0.4$.
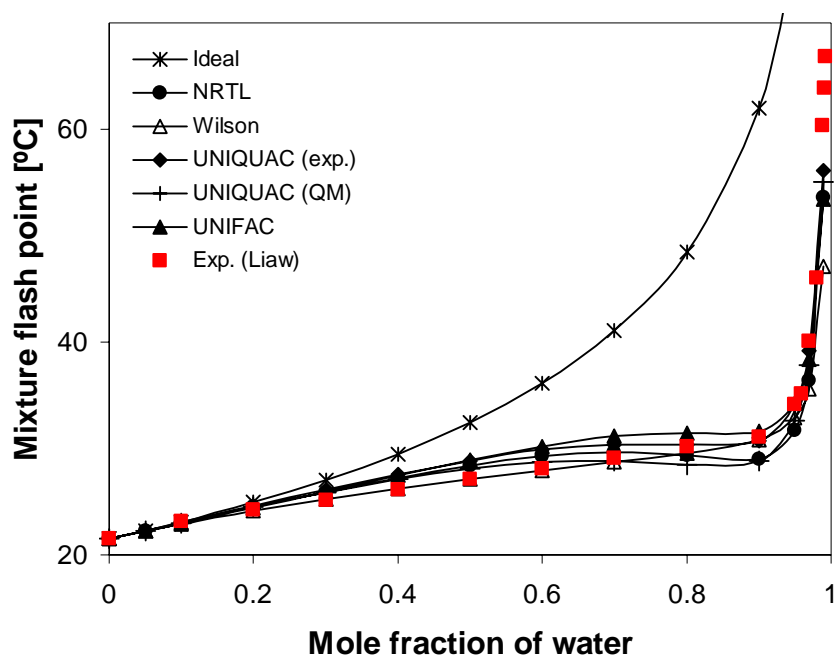
Figure 10. Prediction of the water - 1-propanol mixture flash point.

The G^{ex} model that better agrees with the experimental data is Wilson. UNIFAC gives a little higher result (of about 1 °C) for some compositions but it provides acceptable prediction results.

4.1.4   Water – 2-Propanol

The flash point of pure 2-propanol is 12 °C according to NFPA 325[12]. However, the experimental flash point of 2-propanol obtained by Liaw *et al.*[30] is 13 °C, which is the flash point value selected in this work for all predictions. The difference in flash point data might be attributable to differences in the standard test method or due to the presence of impurities in the sample used. An 87.9% isopropanol solution has a flash point of 14 °C.[12] The parameters used in each G^{ex} model for the calculation of activity coefficients needed for the flash point predictions are presented in Table 8.

**Table 8. Parameters Used in the G^{ex} Models for the Flash Point Prediction of the Water - 2-Propanol Mixture**

G^{ex} model	Parameters			Reference
	A_{12}	A_{21}	α_{12}	
NRTL	869.00	352.79	0.45	49
Wilson	650.35	380.59	-	49
UNIQUAC	-41.70	283.10	-	49

NRTL equation: $A_{12} = (g_{12} - g_{22})/R$, $A_{21} = (g_{21} - g_{11})/R$; Wilson equation: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$; UNIQUAC equation: $A_{12} = (u_{12} - u_{22})/R$, $A_{21} = (u_{21} - u_{11})/R$

The predictions for the water – 2-propanol mixture flash point are presented in Figure 11. The G^{ex} model that best represents the experimental data is the UNIQUAC model. NRTL underestimate the mixture T_f values at high water concentrations ($x_1 \geq 0.8$). The Wilson and UNIFAC model give acceptable results for the mixture flash point. However, UNIFAC tends to overestimate the mixture T_f values around $0.5 > x_1 > 0.8$. As for the water – 1-propanol mixture, the ideal solution model predicts higher flash point values for water – 2-propanol mixture for any water mole fraction equal or higher than $x_1 = 0.4$
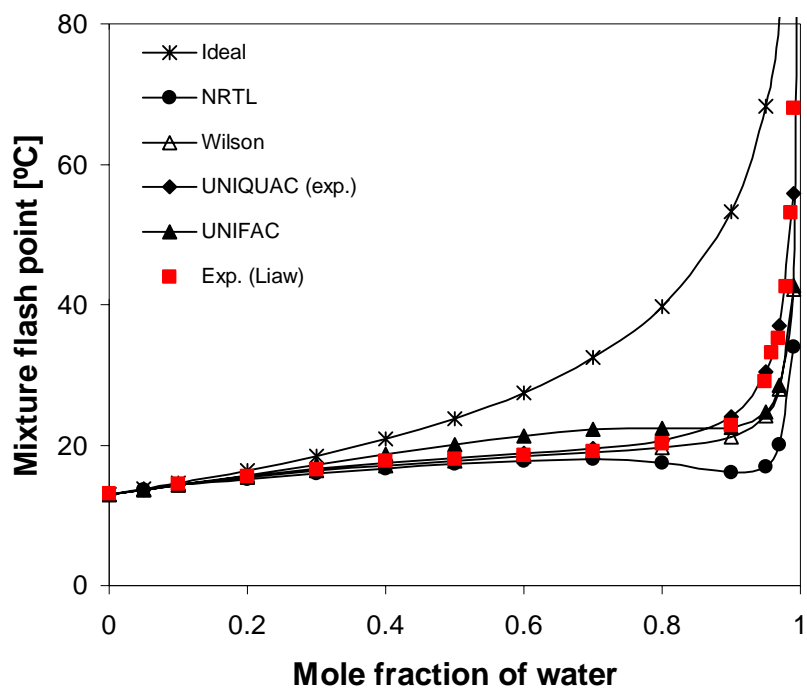
Figure 11. Prediction of the water - 2-propanol mixture flash point.

4.2 FLAMMABLE MIXTURES

These are binary mixtures in which both components are flammable. Background information on these mixtures is provided in section 2.2.2.2 of Chapter II.

4.2.1 Chlorobenzene - Aniline

The flash points of chlorobenzene and aniline are 28 °C and 70 °C, respectively, according to NFPA 325.[12] The experimental data for this mixture were measured at PVAMU.   More than one experimental measurement was taken per mixture composition, and an average T_f value was selected as the mixture flash point. Standard deviations are presented as uncertainties of the experimental data. The parameters used in each G^{ex} model for the calculation of activity coefficients needed for the flash point predictions are presented in Table 9.

Table 9. Parameters Used in the G^{ex} Models for the Flash Point Prediction of the Chlorobenzene - Aniline Mixture

G^{ex} model	Parameters			Reference
	A_{12}	A_{21}	α_{12}	
NRTL	471.6784	-74.1966	0.3006	56
Wilson	-34.2767	433.3115	-	56
UNIQUAC	239.5590	-91.8734	-	56

NRTL equation: $A_{12} = (g_{12} - g_{22})/R$, $A_{21} = (g_{21} - g_{11})/R$; Wilson equation: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$; UNIQUAC equation: $A_{12} = (u_{12} - u_{22})/R$, $A_{21} = (u_{21} - u_{11})/R$

This mixture is nearly ideal and its larger activity coefficient at 298.15 K is 3.34,[57] which means that it slightly deviates from Raoult's law. This mixture is not expected to exhibit MFPB because it is a nearly ideal liquid mixture. The flash point predictions for the chlorobenzene - aniline mixture are presented in Figure 12.
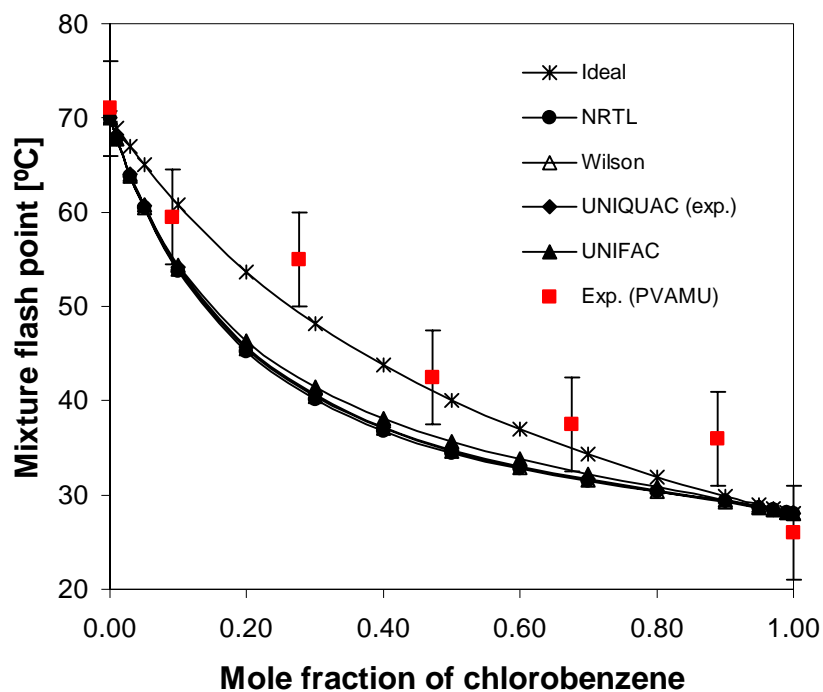
Figure 12. Prediction of the chlorobenzene - aniline mixture flash point.

All G^{ex} models agree in their flash point predictions, even UNIFAC with no experimental BIP's. The experimental data have a lot of uncertainty, however this mixture is nearly ideal and a T_f value lower than the T_f values of the pure components is not obtained. The largest difference in T_f values between the ideal flash point predictions and those obtained with any of the G^{ex} models is 7 °C.

4.2.2   Ethanol – Aniline

The flash points of ethanol and aniline are 13 °C and 70 °C, respectively, according to NFPA 325.[12] The experimental data of this mixture was measured at PVAMU.   More than one experimental measurement was taken per mixture composition, and an average T_f value was selected as the mixture flash point. Standard deviations are presented as uncertainties of the experimental data. The parameters used in each G^{ex} model for the calculation of activity coefficients needed for the flash point predictions are presented in Table 10.

Table 10. Parameters Used in the G^{ex} Models for the Flash Point Prediction of the Ethanol - Aniline Mixture

G^{ex} model	Parameters			Reference
	A_{12}	A_{21}	α_{12}	
NRTL	679.8036	538.0489	0.2925	56
Wilson	862.9016	598.5729	-	56

NRTL equation: $A_{12} = (g_{12} - g_{22})/R$, $A_{21} = (g_{21} - g_{11})/R$; Wilson equation: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$;

This mixture is nearly ideal and it is not expected to exhibit MFPB. The flash point predictions for the ethanol - aniline mixture are presented in Figure 13. The NRTL and Wilson predicted values are lower than the experimental values measured. UNIFAC is the G^{ex} model that best simulates the experimental data; however for some mixture compositions it predicts higher T_f values. The largest difference between the UNIFAC predicted values and the experimental data is 5 °C. The ideal solution model predicts as much as 10 °C above the experimental values.
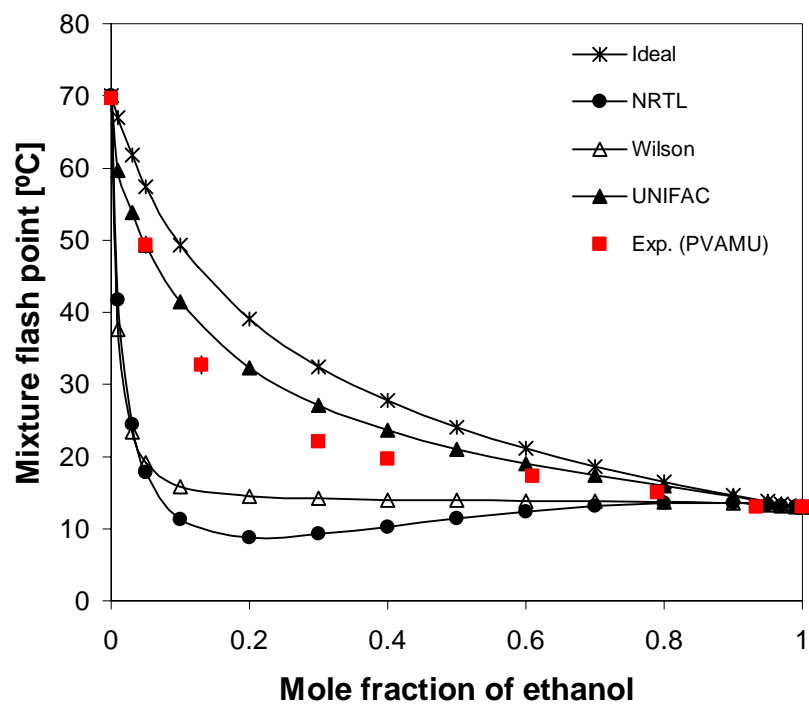
Figure 13. Prediction of the ethanol - aniline mixture flash point.

4.2.3   Octane – Methanol

The flash points of n-octane and methanol are 13 °C and 11 °C, respectively, according to NFPA 325.[12]   The experimental data for this mixture are from the MS thesis of Larson[33], who reported a flash point value of 10 °C and 14 °C for n-octane and methanol, respectively. These are the pure component flash point values used for the prediction calculations.

No BIP's for this mixture were found for any of the G^{ex} models presented in Table 2. The mixture flash point values were predicted with UNIFAC, and the results are presented in Figure 14.

The UNIFAC model does a good job predicting the MFPB of this mixture. It seems to disagree with the experimental data at higher concentrations of octane; however the uncertainties of the experimental data are not known. Besides that, UNIFAC is able to predict the lowest flash point values that can be obtained with this solution.

Large differences in predicted flash point values are obtained with the ideal and non-ideal solution. Differences as large as 12 °C occur between the ideal solution predicted values and the experimental data.

Figure 14. Prediction of the octane - methanol mixture flash point.

4.2.4   Octane – Ethanol

The flash points of both pure n-octane and ethanol is 13 °C according to NFPA 325.[12] Other sources have reported a flash point of 15 °C for n-octane, which is the flash point value selected in this work for all predictions. This mixture is strongly non-ideal, and it was classified as a possible mixture with MFPB according to Liaw's rules[15] (see section 3.2).

The G^{ex} models used in the flash point predictions of this mixture are NRTL and UNIFAC. The binary interaction parameters used in the NRTL model are presented in Table 11.

Table 11. BIP's Used in the NRTL Model for the Flash Point Prediction of the Octane - Ethanol Mixture

G^{ex} model	Parameters			Reference
	A_{12}	A_{21}	α_{12}	
NRTL	604.97	651.91	0.47	[58]

NRTL equation: $A_{12} = (g_{12} - g_{22})/R$, $A_{21} = (g_{21} - g_{11})/R$

The experimental data used to compare the flash point predicted values are from Liaw *et al.*[22] The flash point predictions for the octane – ethanol mixture are presented in Figure 15. This mixture exhibits a depression in the flash point value for almost the entire mixture composition ($0.1 < x_1 < 0.9$). This behavior is well represented with NRTL and UNIFAC models. The NRTL model represents better the experimental data; however, UNIFAC based on theoretical parameters provides acceptable results.

This mixture proves wrong the idea that mixing a chemical with another chemical with higher flash point value the mixture flash point will necessarily increase. In this case, both chemicals have similar flash point values; however a decrease in the mixture flash point is exhibited when they are mixed. This is due to the big differences in size as well as in polarities in these two chemicals, which produce strong repulsion interactions

and high vapor pressures. The ideal solution model predicts flash point values as high as 10 °C above the experimental data.
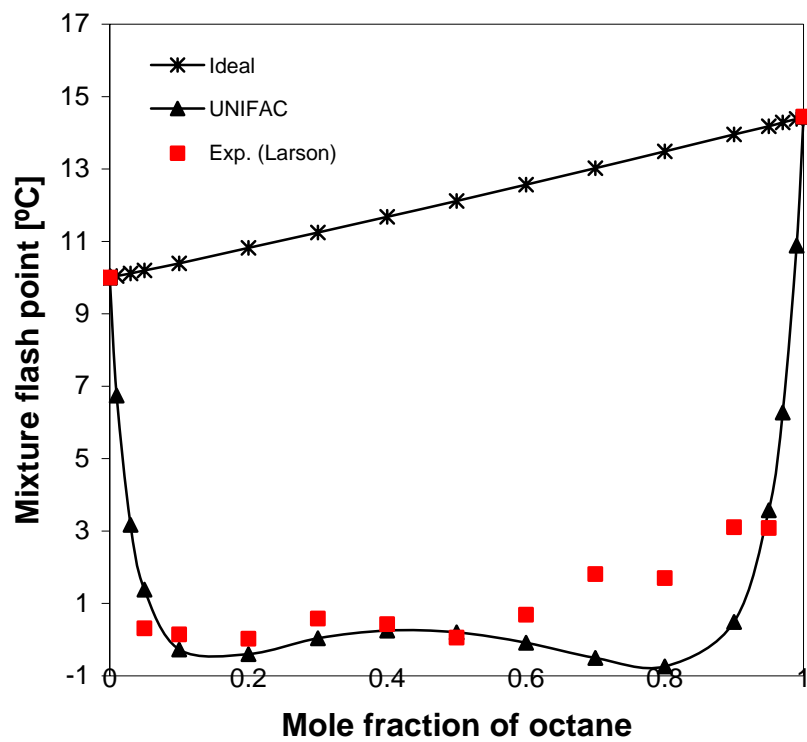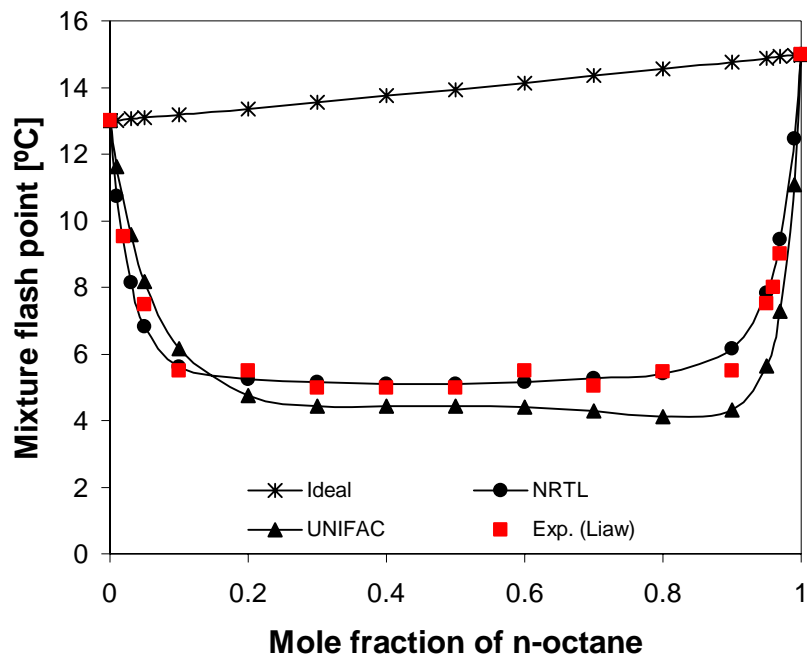

Figure 15. Prediction of the octane - ethanol mixture flash point.

4.2.5   Octane – 1-Butanol

The flash points of pure n-octane and 1-butanol are 13 °C and 37 °C, respectively.[12] Other sources have reported a flash point of 15 °C for n-octane, which is the flash point value selected in this work for all predictions. This mixture is non-ideal and it was classified as a possible mixture with MFPB according to Liaw's rules[15] (see section 3.2).

The G^{ex} models used in the flash point predictions of this mixture are Wilson and UNIFAC. The binary interaction parameters used in the Wilson model are presented in Table 12.

Table 12. BIP's Used in the Wilson Model for the Flash Point Prediction of the Octane - Ethanol Mixture

G^{ex} model	Parameters		Reference
	A_{12}	A_{21}	
Wilson	114.33	667.10	59

Wilson equation: $A_{12} = \left(\lambda_{12} - \lambda_{11}\right)/R$, $A_{21} = \left(\lambda_{21} - \lambda_{22}\right)/R$

The experimental data used to compare the flash point predicted values are from Liaw *et al.*[22] The flash point predictions for the octane – ethanol mixture are presented in Figure 16. This mixture exhibits MFPB around an octane composition of $x_1 = 0.9$. This behavior is well represented with Wilson and UNIFAC models. The difference between the flash point value from ideal behavior and experimental data is approximately 12 °C around an octane composition of $x_1 = 0.2$.
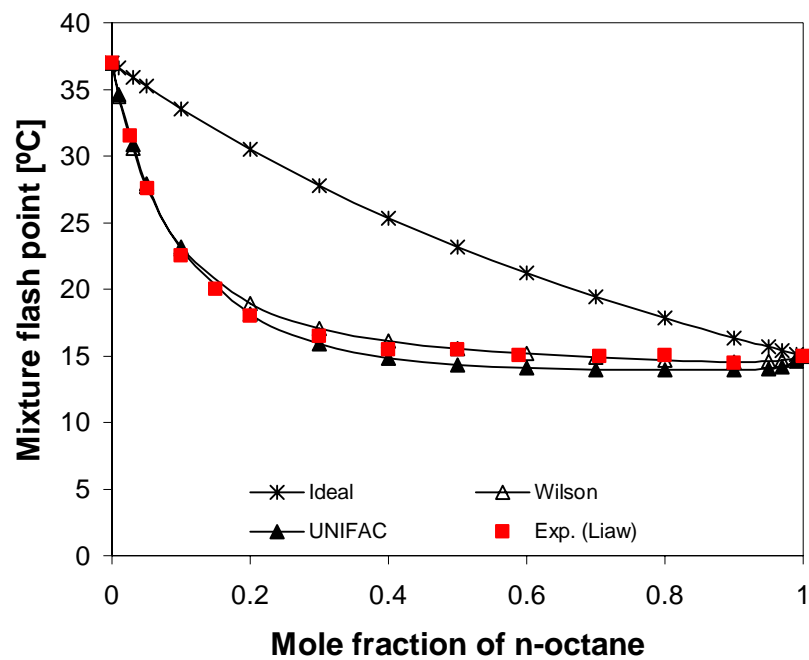
Figure 16. Prediction of the octane - 1-butanol mixture flash point.

4.2.6   Methylacrylate – Methanol

The flash points of methylacrylate and methanol are -3 °C and 11 °C, respectively, according to NFPA 325.[12]   The experimental data for this mixture are from Liaw *et al.*[15], who reported a flash point value of -2 °C and 10 °C for methylacrylate and methanol, respectively. These are the pure component flash point values used in the prediction calculations.

The G^{ex} models used in the flash point predictions of this mixture are NRTL, Wilson, and UNIFAC. The binary interaction parameters used are presented in Table 13.

Table 13. Parameters Used in the G^{ex} Models for the Flash Point Predictions of the Methylacrylate - Methanol Mixture

G^{ex} model	Parameters			Reference
	A_{12}	A_{21}	α_{12}	
NRTL	164.89	214.37	0.2484	60
Wilson	-49.467	468.17	-	60

NRTL equation: $A_{12} = (g_{12} - g_{22})/R$, $A_{21} = (g_{21} - g_{11})/R$; Wilson equation: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$

The flash point predictions for the methylacrylate – methanol mixture are presented in Figure 17. This mixture exhibits MFPB around methylacrylate compositions of $0.6 < x_1 < 0.9$. This behavior is well represented with all G^{ex} models. Predictions obtained with the NRTL and Wilson models are very similar. Flash point predictions obtained with the UNIFAC model agree with the experimental data.

The ideal solution model predicts flash point values as much as 6 °C above the experimental data.
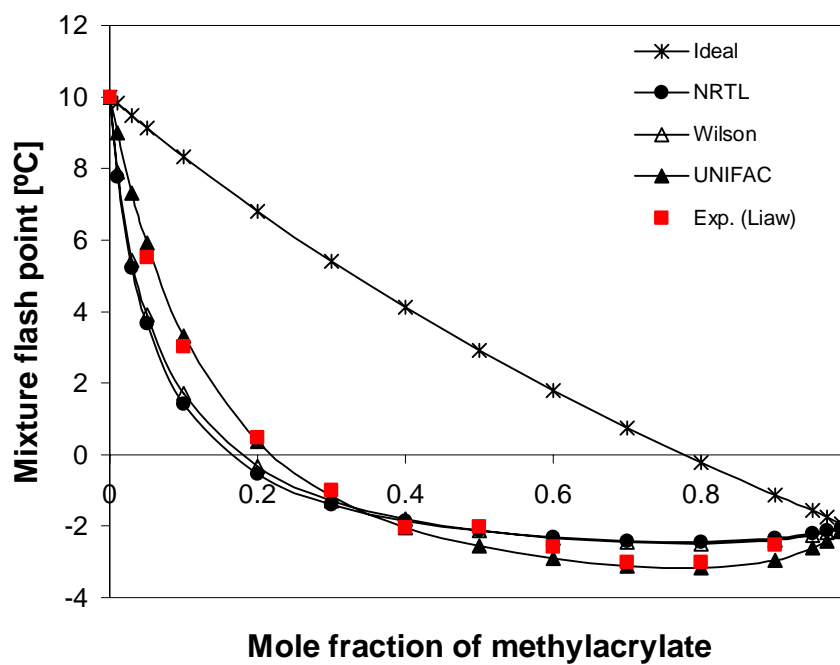
Figure 17. Prediction of the methylacrylate - methanol mixture flash point.

4.2.7 Nitromethane – Ethanol

The flash points of nitromethane and ethanol are 35 °C and 13 °C, respectively, according to NFPA 325.[12] The experimental data of this mixture was measured at PVAMU. More than one experimental measurement was taken per mixture composition and an average T_f value was selected as the mixture flash point. Standard deviations are presented as uncertainties of the experimental data.

The G^{ex} models used in the flash point predictions of this mixture are Wilson and UNIFAC. The Wilson binary interaction parameters used are presented in Table 14.

Table 14. Parameters Used in the G^{ex} Models for the Flash Point Predictions of the Nitromethane - Ethanol Mixture

G^{ex} model	Parameters		Reference
	A_{12}	A_{21}	
Wilson	791.27	850.76	56

Wilson equation: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$

The flash point predictions for the nitromethane – ethanol mixture are presented in Figure 18. This mixture exhibits a slight MFPB at low nitromethane compositions ($x_1 \approx$ 0.2). This behavior is well represented with both G^{ex} models. Flash point predictions obtained with the UNIFAC model agree with the experimental data.

The ideal solution model predicts flash point values as much as 10 °C above the experimental data.
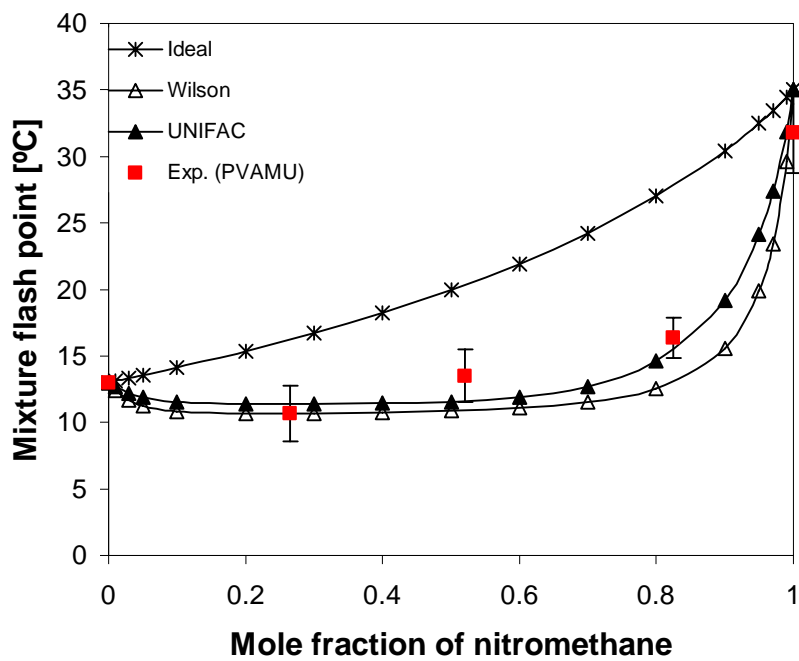
Figure 18. Prediction of the nitromethane - ethanol mixture flash point.

4.2.8   Heptane – Ethanol

The flash point of pure heptane and ethanol are -4 °C and 13 °C according to NFPA 325.[12] The experimental data for this mixture are from the MS thesis of Larson[33], who reported a flash point value of -6.3 °C and 13.3 °C for heptane and ethanol, respectively. These are the pure component flash point values used for the prediction calculations.

The G^{ex} models used in the flash point predictions of this mixture are Wilson, UNIQUAC, and UNIFAC. The binary interaction parameters used are presented in Table 15.

Table 15. Parameters Used in the G^{ex} Models for the Flash Point Prediction of the Heptane - Ethanol

G^{ex} model	Parameters		Reference
	A_{12}	A_{21}	
Wilson	462.5183	1907.4654	61
UNIQUAC	1109.8209	-142.8457	61

Wilson equation: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$; UNIQUAC equation: $A_{12} = (u_{12} - u_{22})/R$, $A_{21} = (u_{21} - u_{11})/R$

The flash point predictions for the heptane – ethanol mixture are presented in Figure 19. This mixture exhibits a depression in the flash point values for almost the entire mixture composition ($0.1 < x_1 < 0.9$). This behavior is well represented with all models. The model that best agrees with the experimental data is the Wilson model. UNIFAC gives acceptable prediction results for most compositions, and it successfully predicts the MFPB.   The UNIQUAC gives good prediction results except at high heptane compositions ($x_1 > 0.9$). The ideal solution model predicts flash point values as much as 17 °C above the experimental data.
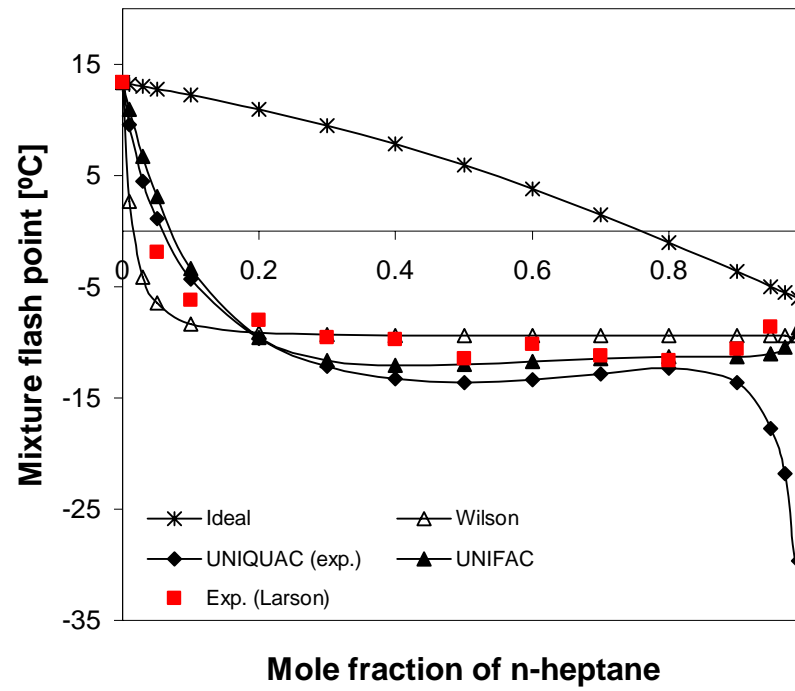
Figure 19. Prediction of the heptane - ethanol mixture flash point.

4.2.9   2-Nitropropane – Octane

The flash point of 2-nitropropane and n-octane are 24 °C and 13 °C respectively, according to NFPA 325.[12]   These flash point values are closed cup values.   The experimental data of this mixture are from the *Journal of Coatings Technology,*[31] which reports open cup flash point values. The closed cup flash point values are lower than the open cup values because the vapors are prevented from escaping.

The only G^{ex} model used in the flash point predictions was UNIFAC; because no BIP's were found for the other models. Predictions were performed using both open and closed cup flash point values and are presented in Figure 20.

In general, UNIFAC predicts satisfactorily the open cup flash point data for the entire mixture. The difference between the open cup flash point experimental data and the predicted values is not larger than 2 °C. This mixture shows the lowest minimum flash point value around a 2-nitromethane composition of 0.4 and 0.6. The largest difference in the flash point values from ideal behavior and experimental data is approximately 9 °C.

Closed cup flash point experimental data were found only for the pure components. Those values were used to obtain the closed cup mixture flash point prediction presented in Figure 20.

Figure 20. Prediction of the 2-nitropropane - octane mixture flash point.

4.2.10   2-Nitropropane – Butanol

The flash point of 2-nitropropane and n-butanol are 24 °C and 37 °C, respectively, according to NFPA 325.[12]   These flash point values are closed cup values.   The experimental data of this mixture are from the *Journal of Coatings Technology*[31] which reports open cup flash point values. The closed cup flash points values are lower than the open cup values because the vapors are prevented from escaping.

The only G^{ex} model used in the flash point predictions was UNIFAC because no BIP's were found for the other models. Predictions were performed using both open and closed cup flash point values and are presented in Figure 21.

In general, UNIFAC predicts satisfactorily the open cup flash point data for the entire mixture, and it represents the MFPB. The difference between the experimental data and the predicted values is not larger than 2 °C. The largest difference in the flash point values from ideal behavior and experimental data is approximately 10 °C.

Closed cup flash point experimental data were found only for the pure components. Those values were used to obtain the closed cup mixture flash point prediction presented in Figure 21.
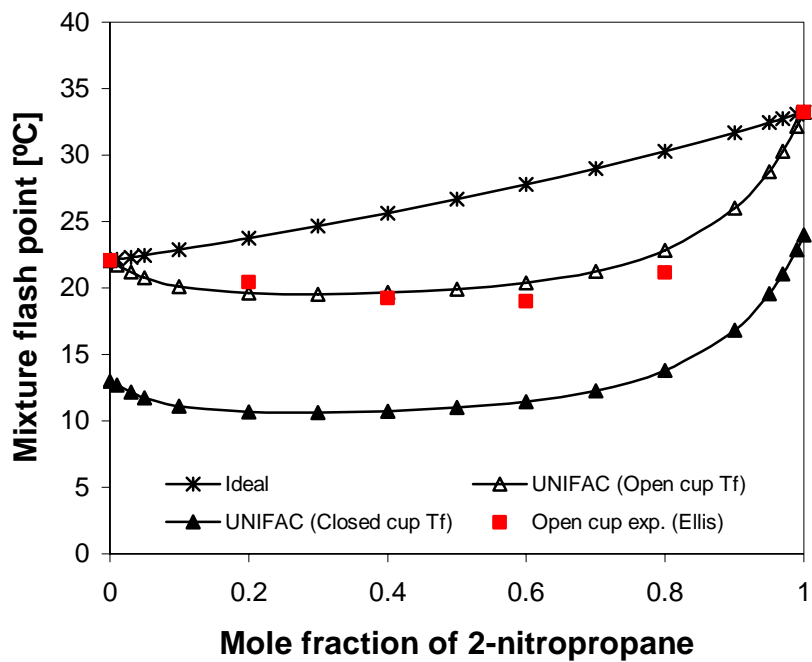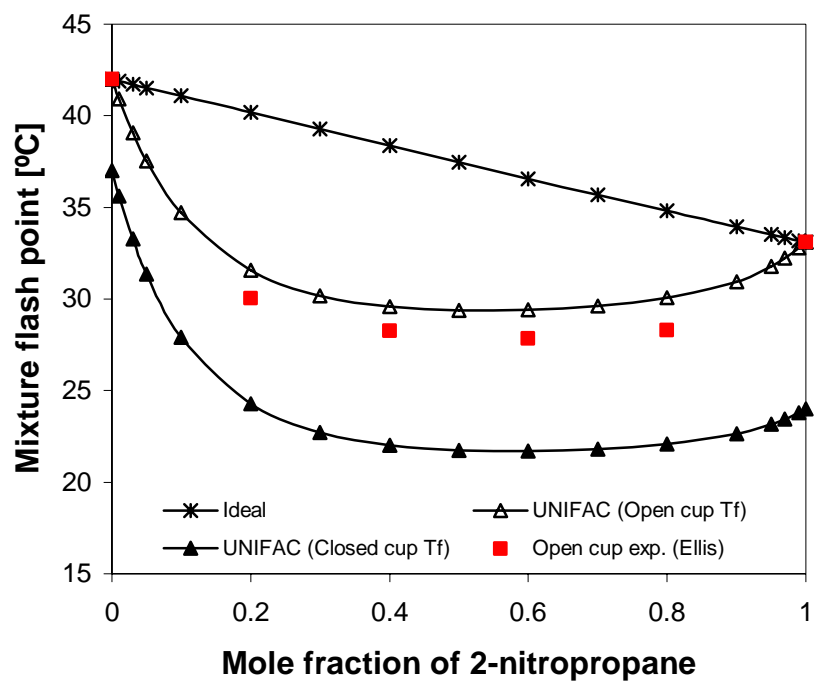
Figure 21. Prediction of the 2-nitropropane - butanol mixture flash point.

CHAPTER V

FLAMMABLE MIXTURES AND THE APPLICATION OF INHERENT SAFETY PRINCIPLES

This chapter discusses the concept of inherent safety and its application to flammable mixtures. Inherent safety is based on the use of technologies and chemicals that reduce or eliminate the possibility of incidents by reducing or eliminating the hazards. Is it possible to make a flammable mixture inherently safer? Is not flammability an inherent property of chemicals? The answers to these questions are presented in this chapter.

Flammability is usually evaluated by a score or index, as for example the Dow Fire and Explosion Index (F&EI)[62], but this evaluation is usually based on pure chemicals because for mixtures the most hazardous component is considered for the evaluation. The F&EI is based on the Material Factor (MF), which is a measure of the intrinsic rate of potential energy release from fire or explosion. The higher the index or score the more hazardous the material. Therefore, the goal of this chapter is to identify which inherent safety principles can be applied to the flammability of binary liquid mixtures.

The effect on the flash point values of three binary mixtures in which octane is the solute is investigated and discussed. Octane is combined with three different solvents, all of them alcohols. All the prediction calculations were performed using the G^{ex} model UNIFAC.

5.1 INHERENT SAFETY

Inherent safety is a design approach useful to remove or reduce hazards at the source instead of controlling them with add-on protective barriers. However, inherent safety is based on qualitative principles that are difficult to evaluate and analyze. The principles upon which inherently safer design is based are:[63]

- *Intensification*: Reduction of inventories of hazardous materials.

- *Substitution*: Replacement of the chemical substances by less hazardous chemicals.

- *Attenuation*: Reduction of the quantity of hazardous materials required in the process. Design processes working at less dangerous processing conditions by reducing temperature, pressure, flow, etc.

- *Limitation of effects*: The facilities must be designed in order to minimize the effects of the release of hazardous chemicals or energies.

When a plant is designed to reduce or eliminate hazards, not only does it become safer but possible emissions to the environment are also reduced or eliminated. Environmental damage resulting from the release of chemicals during an incident can be significantly reduced. During the earlier stages of plant design, it is sometimes possible to choose the safer chemicals to have an inherently safer plant. The idea of safer chemical is usually based on toxicity, reactivity, and flammability.

A liquid that exhibits a flash point value below ambient temperature and which can give rise to flammable mixtures under ambient conditions is generally considered to be more hazardous than one reflecting a higher flash point value.[13] Following the same logic, liquids with high boiling point temperatures are preferred over low boiling point liquids. In general, any liquid with flash point or boiling point temperatures lower than ambient temperature constitutes a major fire hazard than a liquid with values above ambient temperature. Therefore, liquids with high flash point or boiling point temperatures are inherently safer.

5.2 GUIDELINES THAT CAN BE APPLIED

The principle of inherent safety that best applies to flammable mixtures is **substitution**, which means the replacement of a hazardous substance by a less hazardous one. In the case of flammable mixtures, a mixture that exhibits MFPB is by far more hazardous than a mixture that does not exhibit MFPB.

MFPB is a characteristic of non-ideal mixtures with positive deviations from Raoult's law and with minimum boiling point azeotropes. All liquid mixtures that are immiscible and that form azeotropes are minimum boiling. General guidelines that a mixture will form an azeotrope are:

- similar boiling points, and
- the greater the difference in polarity of the components the more likely they will form an azeotrope.

Again these are only guidelines and not rules. However they can be useful in the selection of a solvent and in the prevention of a mixture with MFPB.

The flash point of a mixture is a function of composition and its behavior is highly dependent on the individual components of the mixture. Therefore, substituting one of the components of the mixture will affect the flash point of the mixture. The screening method discussed in Chapter III can be used to eliminate chemicals that will form mixtures with MFPB. In the case that all mixtures exhibit MFPB, the mixture with less flash point depression should be selected as the safer one.

5.3 CAN THE FLASH POINT OF A MIXTURE BE MODIFIED?

Flammability measures the potential to generate fire and explosions, and flash point is the flammability property used to classify or categorize flammable liquids. The flash point of a mixture varies with composition and its behavior strongly depends on the components of the mixture.   Therefore, by changing one of the components of the mixture, the flash point of the mixture is modified.

5.3.1 Criteria

Ideal solutions always have flash point values higher than positive deviation non-ideal solutions. High flash point solutions are considered inherently safer than low flash point solutions. Therefore, the criteria to select the best mixture partner should be based on chemicals that reduce non idealities. The degree of non ideality is measured by activity coefficients.

The idea that mixing a chemical with a high flash point chemical will generate a safer mixture with a high flash point value is erroneous. The interactions between the chemicals of the mixture are the predominant factor that will determine the shape of the mixture flash point curve. How much influence a high flash point component will have in a mixture depends on the interactions between the components that compose the mixture.
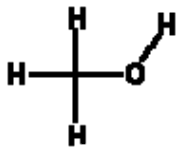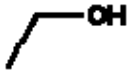
5.3.2 Example: n-octane mixtures

The flash point of three binary mixtures with n-octane as one of the components of the mixture where studied and analyzed. The mixtures considered are:

- octane – methanol,
- octane – ethanol,
- octane – 1-butanol.

The properties of each of these chemicals as reported in NFPA 325[12] are presented in Table 16.

Table 16. Properties of the Chemicals Involved in the Octane Mixtures

Solute	Molecular structure	T_f [°C]	T_b [°C]
n-octane		13	126

Solvents	Molecular structure	T_f [°C]	T_b [°C]
methanol		11	64
ethanol		13	78
1-butanol		37	117

The solute considered is non polar, while all the solvents are polar. These differences in polarities between solute and solvent will produce non-ideal mixtures. The activity coefficients of each mixture at 298.15 K were calculated with the UNIFAC model and are presented in Figure 22.
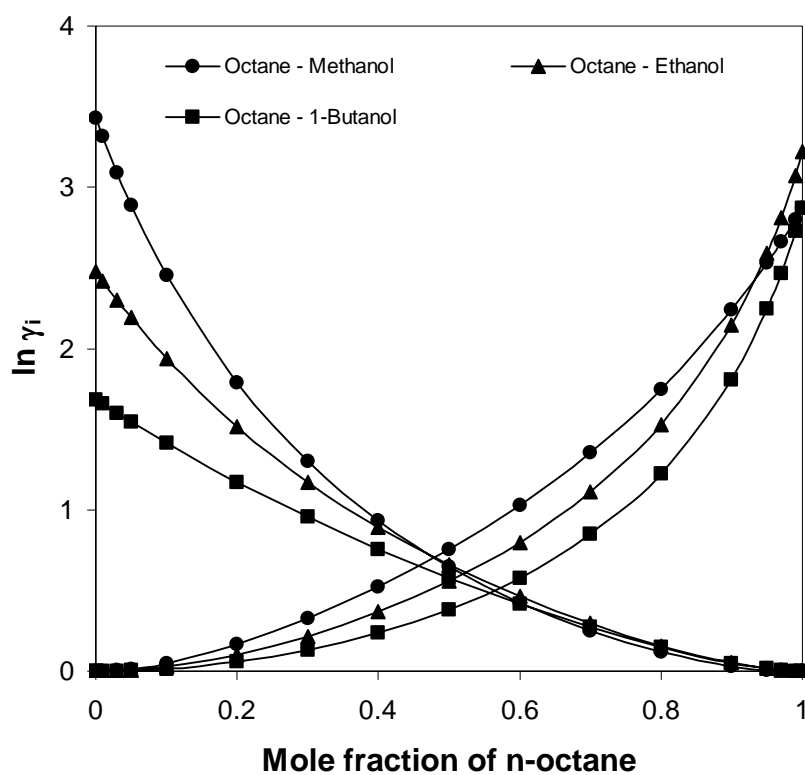
Figure 22. Activity coefficients at 298.15 K calculated with UNIFAC for the n-octane - alcohol mixtures.

The most non-ideal mixture is obtained when octane is mixed with methanol. In this case, all solvents are alcohols differentiated by the addition of a $-CH_2$ group in their chain. The flash point values of each mixture as predicted by UNIFAC are presented in Figure 23.
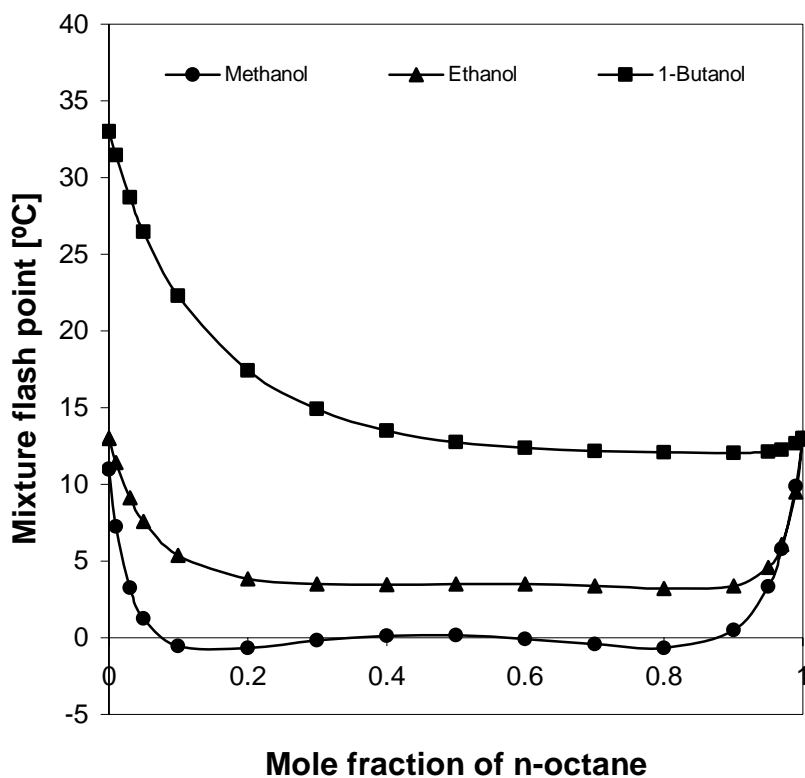
Figure 23. Octane - alcohol mixtures flash point values.

As mentioned before, all octane – alcohols mixtures considered are non-ideal and all of them exhibit MFPB. However, the degree of flash point depression varies with the alcohol considered. When compared with the octane flash point value, the depression in mixture flash point is of approximately 10 °C, 8 °C and 0.05 °C for methanol, ethanol and 1-butanol, respectively.

Octane – 1-butanol should be considered as the inherently safer mixture when compared with the methanol and ethanol mixtures. However, it should be noted that for an octane molar fraction of 0.7 the mixture flash point is about the same as the octane flash point value (13 °C).

CHAPTER VI

CONCLUSIONS AND FUTURE WORK

The procedure developed for the estimation of binary mixture flash point is very useful for the assessment of flammability hazards, because it saves time and effort by providing the user with techniques that can be used to estimate parameters that are needed for the determination of mixture flash point. It also allows for the estimation of the mixture flash point when the experimental data are limited or no experimental vapor-liquid equilibrium data are available for the mixture of interest. Experimental flash point data are always preferred; however even for experiments estimates of the flash point value are needed. The binary mixture flash point procedure provides several resources that can be used to obtain some of the input data needed for the prediction of mixture flash point. Also, a method to predict MFPB is a resource that can be used by the experimenter to perform the experiments in a safer way, since the possibility of having a lower flash point value at a certain composition will not be ignored.

COSMO-RS can be used to estimate mixture component activity coefficients at infinite dilution when the binary interaction parameters are not available. Due to its simplicity COSMO-RS allows for the evaluation and screening of several mixtures at the same time. As a result, more time and effort can be used to analyze mixtures identified as MFPB mixtures.

The calculation of binary interaction parameters from quantum chemical calculations appears to be very promising, even when this approach is still in its early stages. Quantum chemical methods provide valuable tools for performing flammability assessments of mixtures that are hard to test experimentally.

Non-idealities have a strong effect on mixture flash point, and the assumption of ideal solution can lead to wrong estimates that conceal the real risk associated with a

specific mixture. The theoretical UNIFAC group contribution method described very well the MFPB. Therefore, it can be used for the prediction of binary mixtures flash points when the liquid mixture is non-ideal and when the interaction parameters among the mixture components are not available experimentally. This approach provides a great advantage because all the data that are needed to perform the calculations are the vapor pressure as a function of temperature, which can easily be obtained from the Antoine equation or any other method as presented in Chapter III, and the pure flash point value of each of the components of the mixture. All these calculations can be easily performed in an Excel spreadsheet after the functional groups of each component of the mixture have been identified.

The effect of water on the flash point of a flammable component is noticeable only at high water concentrations ($x_1 \geq 0.9$). The flash point of the flammable component is increased only when it is very much diluted in water. When the aqueous mixture contains water concentrations lower than 0.9, it is better to assume that the mixture flash point is equivalent to the flash point of the flammable component.

Highly non-ideal mixtures with positive deviations from Raoult's law have a high tendency to exhibit MFPB, especially if the mixture forms a minimum boiling point azeotrope. A thorough analysis of the flash point of these mixtures should be performed by a combination of experimental and prediction results. Depression of about 10°C can be obtained for the mixture flash point. Therefore, the industrial practice of selecting the component with the lowest flash point value as the flash point of the mixture is not appropriate.

The author suggests the following research topics to extend this work:

- More experimental data for non-ideal binary flammable mixtures and aqueous mixtures are needed. The identification of the combination of specific functional groups with the tendency to form flammable mixtures with MFPB is important. At the same time, it is important to study if water has the same effect on the flash point of other flammable chemicals such as

hydrocarbons. If a series of chemicals from a specific chemical family are tested, some conclusions can be made for that chemical family as a function of chain length or molecular weight. For the group of alcohols studied in this work, the effect of water in the mixture flash point is less noticeable as the alcohol chain is increased.

- Mixture flash point predictions with the UNIFAC model should be performed for non-ideal mixtures with different functional groups to test the flash point prediction capabilities of UNIFAC for various mixtures.

- The work of this dissertation can be expanded by incorporating the modified UNIFAC model. This model differentiates from the original UNIFAC model by using a modified combinatorial part and by incorporating temperature dependent interaction parameters that permit better description of the real behavior (activity coefficients) of mixtures. More information about the modified UNIFAC model can be found in the publication of Gmehling *et al.*[47]

- Mixtures with more than 2 components should be studied experimentally and theoretically. The concept of pseudocomponents, which are lumps of components, can be useful in the flash point predictions. In the case of a 3 component mixture, the 2 components with more effect on the non-ideality of the mixture are recommended as a first guess for the mixture flash point prediction. The prediction results should be validated with experimental data.

- A systematic method to estimate the difference in flash point temperature between ideal and actual as a function of mixture composition should be developed.

$$\Delta T(x_i) = (T_{ideal} - T_{actual})(x_i)$$

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APPENDIX A

EXTENDED ANTOINE EQUATION PARAMETERS

| Chemical | Molecular Formula | Parameters | | | | | T_{Min} | T_{Max} |
		A	B	C	D	E	[K]	[K]
Aniline	C_6H_7N	124.3764	-7.1676E+03	-4.2763E+01	1.7336E-02	5.7138E-15	267.13	699.00
1-Butanol	$C_4H_{10}O$	39.6673	-4.0017E+03	-1.0295E+01	-3.2572E-10	8.6672E-07	183.85	562.93
Chlorobenzene	C_6H_5Cl	19.4343	-2.5801E+03	-3.9391E+00	-4.4005E-11	4.9583E-07	227.95	632.35
Ethanol	C_2H_6O	23.8442	-2.8642E+03	-5.0474E+00	3.7448E-11	2.7361E-07	159.05	516.25
Heptane	C_7H_{16}	65.0257	-3.8188E+03	-2.1684E+01	1.0387E-02	1.0206E-14	182.56	540.26
Methanol	CH_4O	45.6171	-3.2447E+03	-1.3988E+01	6.6365E-03	-1.0507E-13	175.47	512.58
Methylacrylate	$C_4H_6O_2$	47.0416	-3.1218E+03	-1.4860E+01	7.1646E-03	3.4547E-14	196.32	536.00
Nitromethane	CH_3NO_2	35.8372	-3.0979E+03	-9.7786E+00	-4.3921E-10	3.4336E-06	244.60	588.15
2-Nitropropane	$C_3H_7NO_2$	1.2047	-2.3533E+03	4.6729E+00	-1.4843E-02	8.8798E-06	181.83	594.00
Octane	C_8H_{18}	29.0948	-3.0114E+03	-7.2653E+00	-2.2696E-11	1.4680E-06	216.38	568.83
1-Propanol	C_3H_8O	31.5155	-3.4570E+03	-7.5235E+00	-4.2870E-11	1.3029E-07	146.95	536.71
2-Propanol	C_3H_8O	38.2363	-3.5513E+03	-1.0031E+01	-3.4740E-10	1.7367E-06	185.28	508.31

APPENDIX B

INSTRUCTIONS FOR THE FLASH AQUEOUS AND FLASH FLAMMABLE EXCEL SPREADSHEETS

1. Enter input data in the yellow cells. Input data needed are: flash point value and extended Antoine parameters for each component of the mixture, and binary interaction parameters for the G^{ex} models (NRTL, Wilson, and UNIQUAC).

Figure 24. Example of the Excel spreadsheet.

2. Input initial guess for the mixture flash point.

3. Go to **Tools→ Goal Seek** to perform the optimization calculation. Follow the instructions presented in the Table below.

Table 17. Goal Seek Input Values

Set cell:	*Select opt cell.*
To value:	*0*
By changing cell:	*Select input T cell.*

APPENDIX C

UNIFAC GROUPS

Chemical	Groups	
	Name	Number of occurrences
Aniline	ACH	5
	ACNH2	1
1-Butanol	CH3	1
	CH2	3
	OH	1
Chlorobenzene	ACH	5
	ACCl	1
Ethanol	CH3	1
	CH2	1
	OH	1
Heptane	CH3	2
	CH2	5
Methanol	CH3OH	1
Methylacrylate	CH2=CH	1
	CH3COO	1
Nitromethane	CH3NO2	1
2-Nitropropane	CH3	2
	CHNO2	1
Octane	CH3	2
	CH2	6

Chemical	Groups	
	Name	Number of occurrences
1-Propanol	CH3	1
	CH2	2
	OH	1
2-Propanol	CH3	2
	CH	1
	OH	1
Water	H20	1

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