Modelling of evaporative losses in n-alcohol/diesel fuel blends

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HIGHLIGHTS

• Modelled evaporative losses from blends agreed with experimental results.
• Diffusion and activity coefficients were proved to have significant effect.
• Evaporation rate was proportional to the decrease in the alcohol carbon number.
• Paradoxically, evaporative losses are faster in blends with lower alcohol content.

ABSTRACT

Alcohol/diesel fuel blends allow reducing the formation of soot in diesel engines. However, its use in a large scale framework still faces the challenge of high evaporative losses under storage conditions which is hindered by the high volatility of the alcohols. Since the design of the most adequate fuelling system for each blend requires detailed knowledge about the evaporation losses from the liquid phase, in this work a method for calculating the evaporation of pure n-alcohols (from C1 to C5 carbon atoms) and blends of these alcohols with ultra-low sulphur diesel (ULSD) was proposed. Alcohols vapour pressure was determined with the Antoine equation, while the diffusion coefficient of alcohols in air was calculated as a function of carbon number and temperature. The coefficients of activity were obtained by the combination of continuous thermodynamic (gamma distribution function) and a modified UNIFAC-Dortmund-Continuous method. The evaporation losses model is based on Fick's law and exhibited good agreement with experimental data for all alcohols and blends at 20% content of all alcohols and at 20–60% contents of n-butanol with diesel fuel. The evaporation was found to decrease approximately with an inversely proportional rate with respect to the increase in the carbon chain length of the alcohol. The paradox of faster evaporative losses from blends with lower alcohol content is explained.

1. Introduction

Blending diesel fuels with bioalcohols is one of the most efficient means to introduce a renewable fraction in the fuel, to improve its sustainability, and to provide some oxygen content, this being essential to reduce soot engine emissions. Additionally, compared with biodiesel/diesel blends, alcohol/diesel (or even alcohol/biodiesel/diesel blends) can provide similar renewable fraction, similar oxygen content and superior soot-reduction potential with much lower cost and energy consumption. The hydroxyl group of the alcohol molecules contributes to reduce soot formation, and consequently particulate emissions, even more than other functional groups with the same oxygen content [1–3], especially at high engine loads [4,5]. However, different challenges will have to be faced for the future extension of the use of these alcohols as diesel fuel components to a large scale.

First, the energy and environmental life-cycle assessments of the bioalcohols must be advantageous with respect to other biofuels. The recent commitments to further reduce greenhouse emissions from transportation sources make this a crucial factor. Ethanol has proved to have a significant potential for reducing life-cycle greenhouse gas emissions, as acknowledged by the European directive 28/2009/CE [6], where the typical greenhouse savings range from 21% (in the case of using wheat as feedstock) to 75% (in case of sugar cane ethanol) or even to 87% (in case of wheat straw). Methanol is also gaining interest as a renewable fuel, since its production derived from gasification of waste biomass followed by catalytic synthesis at high pressure provides both high yield (45–55% in weight) and energy efficiency (70–75%) [7]. Biomass

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sources are even preferable for biomethanol production than for bioethanol because the last is a high-cost and low-yield product [8,9]. Butanol has also proved to have an interesting potential for saving life-cycle greenhouse emissions when it is produced from acetoxybutylicum fermentation, as far as the bio-acetone obtained as co-product is valued as such [10]. Other higher alcohols could also become a sustainable alternative as far as they can be produced in biorefineries together with a wide range of commodities.

Second, the fuel storage and handling difficulties derived from the high volatility of alcohols must be addressed. Previous experiences with ethanol–diesel blends have proved that different technical modifications in the fuelling system are necessary, such as the installation of seals for fuel tanks, security valves on both vehicle fuel tanks and fuel station tanks, and special systems for recovering of fuel vapours on vehicles and fuel stations and to avoid vapour locks. These restrictions constitute a barrier for the massive use of these blends in private vehicles, and have limited their practical use to captive fleets, such as those of urban buses or public construction and civil machinery.

Third, some key properties of the alcohol blends affecting the injection system may limit their use beyond certain limits. A previous work was published studying blending stability, lubricity, viscosity and cold filter plugging point as the key properties of alcohol–diesel blends [11].

Finally, among the properties affecting the combustion process, cetane number is certainly the most limiting one. Although diesel engines need to be fuelled with high cetane number-fuels (above 51 as stated by norm EN 590) to facilitate autoignition and provide short ignition delay, alcohols exhibit low cetane numbers [12,13]. For this reason, the direct use of alcohols as fuels for unmodified diesel engines is not recommended, unless they are blended with diesel fuel. However, long-chain alcohols have higher cetane number than short-chain alcohols [14,15], this enhancing their interest for being used in diesel engines.

The work presented here is related to the second challenge mentioned. The design of the most adequate fuelling system for each blend requires detailed knowledge about the evaporation losses from the liquid phase. This work proposes a model to predict evaporation losses from alcohols (from methanol to n-pentanol) blended with a diesel fuel under stagnant air conditions, and describes the guidelines to be followed for modelling evaporative losses from other base fuels and under more realistic evaporation conditions.

Although some literature has reported modelling studies on vapour pressure and evaporation losses in alcohol–gasoline blends [16] or in biodiesel–diesel blends [17], very few have been found addressing this issue in alcohol–diesel blends, and in any case, these studies have been applied to droplet evaporation in ethanol–diesel blends from combusting [18] or non-combusting [19] liquid sprays, rather than to evaporation losses from fuel storage systems.

2. Tested fuels, blends and experimental conditions

2.1. Pure fuels

The main measured specifications of pure alcohols and ULSD are shown in Table 1. The diesel reference fuel was supplied by the Colombian petroleum company (Ecopetrol). The alcohols used in this work were methanol (Honeywell, 99.9% purity), ethanol (Panreac, 99.5% purity), n-propanol (Merck, 99.5% purity), n-butanol (Panreac, 99.5% purity), and n-pentanol (Panreac, 98% purity).

2.2. Blends

Blends of 20% by volume of the five n-alcohols in ULSD fuel were selected to experimentally validate the evaporation model. Additionally, blends of n-butanol with 30%, 40%, 50% and 60% content in diesel fuel were also selected to study the effect of the alcohol content in the evaporation losses. The volume, mass and mole fractions of each alcohol (identified with subscript A) in each blend were selected to study the effect of the alcohol content in the evaporation losses. The volume, mass and mole fractions of each alcohol (identified with subscript A) in each blend were selected to experimentally validate the evaporation model.

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Evaporation losses directly depend on the concentration of vapour on the liquid–gas interphase, which are related to the vapour pressure of the volatile compounds (i.e., alcohols). The determination of the vapour pressure \( p_{\text{v,A}} \) was made by means of the Antoine equation, with \( p_{\text{v,A}} \) in Pa and temperature in K:

\[
\log p_{\text{v,A}} = A - \frac{B}{C + T}
\]  

(1)

Coefficients \( A, B \) and \( C \) are specific for each alcohol and are collected in different data bases, where often different values are distinguished as a function of the temperature range. The data used in this work are shown in Table 3. Fig. 1 presents \( p_{\text{v,A}} \) as a function of temperature for all alcohols.

3.2. Diffusion coefficients

The correlation proposed by Lapuerta et al. [25] for the determination of the diffusion coefficients of alcohols in their binary alcohol–air gaseous mixtures at reduced pressure, was used (Eq. (2)), with \( n \) being the carbon number of the alcohols. Results showed that diffusion coefficients are higher as carbon chain length decreases, as shown in Fig. 2.

\[
\ln D_{\text{Ai,Ar}} = (5.386 - 0.686n) \ln T - (32.138 - 3.604n)
\]  

(2)

3.3. Activity coefficients

Continuous thermodynamic theory and modified UNIFAC method were combined to calculate the coefficients of activity of the n-alcohols/diesel blends following the methodology described in Ref. [26]. The variation of activity coefficients with of the alcohol content in blends is shown in Fig. 3. From this figure, two conclusions can be obtained:
The values of the activity coefficients decrease, almost exponentially, from diesel fuel (nil alcohol content) to blends with twenty percent of alcohol. From this point, the variation of activity coefficients is smaller as the alcohol content increases, and they tend to unity for pure alcohols.

Activity coefficients are higher for longer chain-length alcohol, although the differences between alcohols remain small for blends with high alcohol content.

### 4. Evaporative losses model

#### 4.1. Vapour–liquid equilibrium condition

In multi-component and multi-phase systems, the equilibrium condition is expressed by the equivalence between the fugacity of each component in each phase and the fugacity of that component in every other phase. In the case of liquid–vapour equilibrium of diesel–alcohol blends, since the vapour pressure of diesel fuel is very low in comparison with the alcohols, only the equivalence between the fugacity of the alcohol in the liquid and vapour phases is considered:

$$f_v^A = f_l^A$$

The fugacity of the alcohol component in the vapour phase is related to the coefficient of fugacity ($\phi_v^A$) and to its mole fraction in the vapour phase ($x_v^A$) through Eq. (4):

$$f_v^A = \phi_v^A \cdot x_v^A \cdot p$$

In the liquid phase, the fugacity of alcohol component is related to its activity coefficient ($\gamma_l^A$) and to its fugacity when the alcohol is not blended but pure ($f_l^A$):

$$f_l^A = \gamma_l^A \cdot x_l^A \cdot f_l^{0A}$$

The equilibrium condition (Eq. (3)) leads then to:

$$\phi_v^A \cdot x_v^A \cdot p = \gamma_l^A \cdot x_l^A \cdot f_l^{0A}$$

The fugacity of the liquid pure alcohol depends on its vapour pressure. This relationship is shown when the coefficient of fugacity, expressed here as a function of the compressibility factor ($z_A$),

### Table 3

Antoine coefficients for different alcohols, obtained from Refs. [23,24].

<table>
<thead>
<tr>
<th>Antoine coefficient</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>n-Propanol</th>
<th>n-Butanol</th>
<th>n-Pentanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>$T &lt; T_b$</td>
<td>1582.27</td>
<td>1642.89</td>
<td>1690.864</td>
<td>1351.555</td>
</tr>
<tr>
<td></td>
<td>$T &gt; T_b$</td>
<td>1521.23</td>
<td>1332.04</td>
<td>1300.491</td>
<td>1254.502</td>
</tr>
<tr>
<td>C</td>
<td>$T &lt; T_b$</td>
<td>−33.45</td>
<td>−42.85</td>
<td>−51.804</td>
<td>−93.34</td>
</tr>
<tr>
<td></td>
<td>$T &gt; T_b$</td>
<td>−39.15</td>
<td>−73.95</td>
<td>−86.364</td>
<td>−105.246</td>
</tr>
</tbody>
</table>

Fig. 1. Vapour pressure of alcohols as a function of temperature.

Fig. 2. Diffusion coefficients of alcohols in alcohol–air mixtures as a function of temperature.

Fig. 3. Activity coefficients of alcohols in function of mole fraction of alcohol at mole fraction in liquid phase of blends.
is integrated from zero to the ambient pressure surpassing the vapour pressure:
\[
\ln f_A^0 = \ln p + \int_0^p \frac{1}{\rho} \left( z_A - 1 \right) \frac{dp}{p} \\
= \ln p + \int_0^{z_{A,A}} \frac{1}{\rho} \left( z_A - 1 \right) \frac{dp}{p} + \int_{z_{A,A}}^p \frac{1}{\rho} \left( z_A - 1 \right) \frac{dp}{p}
\] (7)

Below the vapour pressure (first integral in Eq. (7)) alcohol is in vapour phase and, at such low pressure, this vapour can be assumed to behave as an ideal gas \((z_A = 1)\), whereas above the vapour pressure (last integral), alcohol is in liquid phase and it can be assumed to be incompressible \((z_A = 0)\). Therefore, Eq. (7) becomes:
\[
\ln f_A^0 = \ln p - \left( \ln p - \ln p_{v,A} \right) \rightarrow f_A^0 = p_{v,A}
\] (8)

Consistently with the last assumptions, the coefficient of fugacity of the alcohol at the vapour phase (with partial pressure remaining below the vapour pressure) must be considered equal to unity. The equilibrium condition (formerly Eq. (6)) leads finally to:
\[
x_A^v = \frac{\gamma_A^v}{\lambda_A \cdot p_{v,A}}
\] (9)

Modelling of the evaporation losses (Section 4.2) requires knowing the mass fraction of alcohol at the interface, \(w_A^v\). This fraction can be obtained by assuming that the vapour phase is just composed of alcohol and air:
\[
w_A^v = \frac{x_A^v \cdot W_A}{W_A \cdot x_A^v + W_{Air} \cdot (1 - x_A^v)}
\] (10)

4.2. Modelling of evaporation losses for alcohols

Mass diffusion of a gaseous component in air is governed by Fick’s law. Assuming that evaporation from a liquid occurs under uniform temperature and pressure with no border effects, the approach can be assumed to be one-dimensional. In this case the Fick’s law for a single component can be written as [27]:
\[
m_{A,L}^w = \frac{\rho^v \cdot D_{A,Air} \cdot \text{d}w_A^v}{\text{d}z}
\] (11)

where \(m_{A,L}^w\) is the mass flow rate per unit area of alcohol (with units kg/s m²) in the vertical direction \((z \text{ m})\), \(D_{A,Air}\) is the binary diffusion coefficient (in m²/s) and \(w_A^v\) is the mass fraction (dimensionless) in the gas phase of the alcohol. \(\rho^v\) is the density of the gaseous mixture obtained with the ideal gas law (in kg/m³, Eq. (12)) with \(R\) being updated as concentration of alcohol in air increases.
\[
\rho^v = \frac{p}{RT}
\] (12)

The model proposed here divides both time and height of the gas volume into finite steps. Since ambient conditions are supposed to remain unchanged along a height step and during a time step, the product \(\rho^v \cdot D_{A,Air}\) can be considered constant for integration. The model integrates along every height step at each time step, and the result for \(w_A^v\) from the previous time step is used at the current one, starting with \(w_A^{v,0}\) at the interface level \((z = 0)\, \text{Fig. 4} \).

This integration provides the mass flow rate transported along a height step of the cylindrical vessel (with diameter \(d\)), \(m_{A,z}\), at a given instant:
\[
m_{A,z} = \frac{\rho^v \cdot \pi d^2 \cdot D_{A,Air}}{4 \cdot \Delta z} \ln \left[ \frac{1 - w_A^v(z)}{1 - w_A^{v,0}} \right]
\] (13)

Initially, the mass flow rate does not remain uniform along the vessel’s height because of the mole of alcohol being accumulated. The evaporation losses can be identified just with the transported alcohol mass flow rate at the interface, \(m_{A,z}\). This looped couple of equations is then solved at each height step for successive time steps until \(z = L\), where alcohol is assumed to reach infinite dilution in air: \(w_A^v(z = L) = 0\). This boundary condition forces the concentration profiles to stabilize after a short period of time. From this instant onwards, the mass flow rate of alcohol transported along the cylindrical vessel (with diameter \(d\)), \(m_{A,z}\), becomes uniform and then it can be identified as the evaporated alcohol mass flow rate. Form this instant onwards, it can be obtained (in kg/s) as:
\[
m_{A} = -\frac{\rho^v \cdot \pi d^2 \cdot D_{A,Air} \cdot \text{ln}(1 - w_A^{v,0})}{4L}
\] (14)

However, even after the process has reached the quasi-stable regime, this mass of evaporated alcohol changes slightly with time because the depth of the interface in the vessel decreases, and thus the height \(L\) increases, as the liquid is being consumed.

The model starts running right after the simple preparation, the initial conditions being \(m_A(t = 0) = 0, L(t_0) = L, w_A^v(z = 0, t = 0) = w_A^{v,0}\) and \(w_A^v(z = z_1, z = z_2, \ldots, z = L, t = 0) = 0\). Then the evaporated mass, the liquid density, the free height of the vessel and the mass fractions of diesel on the alcohols in the liquid phase are successively updated at each instant through:
\[
m_A^v(t_i) = m_A^v(t_{i-1}) + m_{A,0}^v(t_{i-1}) \cdot (t_i - t_{i-1})
\] (15)
\[
\rho^v(t_i) = \frac{1}{w_A^v(t_i) \cdot \frac{w_A^{v,0}}{w_A^{v,0}}}
\] (16)
\[
L(t_i) = L(t_{i-1}) + \frac{m_A(t_{i-1}) - m_A(t_i)}{\rho^v \cdot A}
\] (17)
\[
\rho_A^v(t_i) = \frac{m_A^v(t_i)}{m_A(t_i) + (m_A^v(t = 0) - m_A^v(t_i))}
\] (18)
\[
w_A^v(t_i) = \frac{m_A^v(t = 0) - m_A^v(t_i)}{m_A^v(t = 0) + (m_A^v(t = 0) - m_A^v(t_i))}
\] (19)
In the following time steps, the calculation has to sweep increasing number of height steps, until reaching the top of the vessel, furthermore in the alcohol/diesel blend, the remaining concentration of alcohol in the blend must also be updated. As a consequence, the mole fraction (Eq. (9)) and mass flow (Eq. (14)) of alcohol in the interface decrease in the gas phase. All these variables must be updated at each time step leading to changes in the evaporation mass flow rate (Eq. (15)). The steps followed for the calculation of the evaporative losses are shown in Fig. 5.

5. Results and experimental validation

Fig. 6 shows a comparison between the experimental results of evaporative losses from the n-alcohol/diesel fuel blends (20% of alcohol) and those proposed by UNIFAC-Dortmund-Continuous method. Additionally, results obtained from the ideal method (activity coefficient = 1) are included for each alcohol. The mass of methanol in the blend was completely evaporated at around 10 h, the mass of ethanol at around 20 h and the mass of n-propanol at around 60 h (see Fig. 6). On the contrary, in the case of n-butanol and n-pentanol, after 90 h the alcohol mass was not completely evaporated (scale of y axis is different for the heaviest alcohols), consistently with their lower volatility.

Comparing the methods used, the UNIFAC-Dortmund-Continuous method proposed in this work predicts with qualitatively good accuracy the evaporative losses for all alcohols, with no fitting constants. An approximately inversely proportional relationship can be observed between evaporation rate and carbon chain length of the alcohol. This relationship is illustrated in Fig. 7, where the average evaporation rate along the first eight hours (before the complete evaporation of the lightest alcohol), obtained from both the model and the experiments, is shown. The deviation of the proposed model with respect to the experimental results observed for the cases of methanol/diesel (maximum over-prediction of 35%) and n-pentanol/diesel blends (maximum under-prediction of 38%) could be explained, in the former case, by the error induced during the mass measurement of a very volatile material, and in the latter case, by the not-negligible evaporation of the most volatile fraction of diesel fuel over a very long period of time. For the rest of alcohol–diesel blends, errors remain always below 15%. On the contrary, results provided by ideal model were far from those obtained experimentally, which implies that blends are far from ideal behaviour. These results are consistent with the high values of activity coefficient corresponding to blends with 20% content (or less) of alcohol (Fig. 3).

In order to complete the validation of the model proposed, different blends with a wide range of alcohol contents (with the consequent variation in the activity coefficients) were tested. n-Butanol was chosen for the experiments and it is expected that rest of alcohols would achieve the same agreement since the diffusion and the activity coefficients for the different alcohols are not qualitatively different (Fig. 3). Results for 30%, 40%, 50% and 60% content of n-butanol in blends (additionally to the results for 20% already shown in Fig. 6) are shown in Fig. 8.

**Fig. 5.** Steps of the modelling of evaporation losses for the n-alcohol/diesel blends.
Evaporation rate, defined as the mass evaporated per unit time (slope of lines in Fig. 8), appears to be slightly lower as the butanol content increases. Although this trend could be opposite to the expected one, it is consistent with the increase of activity values as the alcohol content decreases. In Eq. (9), lower values of $x_i^j$ are compensated by the higher values of $\gamma_i^j$. Results from the ideal model in Fig. 8 show that the evaporation rate increases proportionally to the highest butanol content, but this trend is reversed in the UNIFAC-Dortmund-Continuous model and in the experiments because at high butanol concentrations the activity coefficients are close to unity, whereas at low concentrations they are very high (Fig. 3). These results were completed with additional modelling results for all alcohols (not only n-butanol but for all alcohols) and the resulting evaporation rates (again averaged along the first eight hours) are shown in Fig. 9. It can be observed that, for all alcohols, the mentioned compromise between activity coefficient and alcohol content leads to a wide region (starting from 10% or 20% contents) in which evaporation losses decrease as the alcohol content increases. Dotted lines in Fig. 9 indicate unstable blends [11], for which experimental validation is impossible.

As an intermediate result from the model, Fig. 10 shows, as an example, that n-butanol evaporates much faster than ideally and thus, its mole fraction in the liquid phase decreases sharply. The reason for this is that the mole fraction in the vapour interphase increases with time (as the alcohol content in the liquid decreases) rather than decreasing (as predicted by the ideal model), as a consequence of the increase in the activity coefficient.
6. Conclusions

Evaporative losses of different alcohol–diesel blends were studied in this work. Results obtained experimentally were compared with those estimated using a model based on the UNIFAC-Dortmund-Continuous method, proposed in this work. From the results, the following conclusions can be drawn:

- The higher is the volatility of the alcohol, the faster is the evaporation process. The evaporation decreases approximately with an inversely proportional rate with respect to the increase in the carbon chain length of the alcohol. While all the content of methanol, ethanol and n-propanol in blends (20%) was evaporated in 10, 20 and 60 h, respectively, part of n-butanol and n-pentanol remains in liquid blends at the end of the test (almost 100 h).

- The evaporation rate results obtained from the model proposed in this study, which includes no fitting constants, are in a good agreement with the results obtained experimentally. Only a slight underestimation of the evaporation rate for n-pentanol blends can be remarked.

- Results were far from the ideal behaviour for all alcohols, especially for low alcohol contents. As the alcohol content in the blend increases, the activity coefficients get closer to ideal ones
(unity) and both results, experimental and modelled become closer to those corresponding to the ideal model.

- The model was helpful to explain the experimentally observed paradox of low alcohol content blends evaporating faster than high content blends. This effect can be explained as a consequence of a compromise between activity coefficients and alcohol content.

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