Abstract: Ethanol seems to be the biofuel most likely to be used in large quantities in spark ignition (SI) engines. One of the most difficult issues associated with the use of alcohols in SI engines is that cold start capabilities are greatly reduced compared to gasoline operation. This is due to alcohols’ reduced saturation pressure at low ambient temperatures. As a result, gasoline is mixed with ethanol in order to ensure good cold start performance during winter. The paper presents a study of evaporative properties for gasoline, 10, 70 and 85% ethanol mixed with the fossil fuel on a volumetric basis, by using a simple thermodynamic model to predict evaporated fuel fraction. A major conclusion of the study is that gasoline addition to bioethanol greatly improves vapor pressure at low ambient temperatures. Also, more components need to added to the equivalent mixture used to simulate the properties of gasoline, in order to better predict cold start enrichment requirements in port injection SI engines.

Key-Words: bioethanol, gasoline, spark ignition, cold start, thermodynamic model, air–fuel mixture cooling

1 Introduction
Port injection engines feature a complex process of heat and mass transfer during air–fuel mixture formation. Intake air is mixed with pulverized fuel that follows a multi-stage process in which the liquid is broken into small size droplets and then evaporates. How much fuel actually evaporates depends on various conditions such as manifold pressure, air temperature and relative humidity, air–fuel ratio as well as any additional heat flux from surrounding engine components [1].

Even though biofuels sustainability and the actual level of carbon dioxide emissions reduction are still ongoing debates, given the legal framework that mandates the use of renewable energy sources, already in place in many regions, with strategies spanning beyond the next decade [2], there is a need to study the effects of using biofuels in the transport sector.

Ethanol seems to be the bioalcohol most likely to be used in spark ignition (SI) engines, given that it has the advantage of a well known production method and high octane rating [3]. One major issue when using alcohols to fuel SI engines is that cold start during winter proves very difficult, if not even impossible. Bioethanol has been used as a fuel for many years, in regions where ambient temperatures rarely drop below 15 °C. Vehicles equipped to run on pure ethanol (95.6% volumetric concentration or anhydrous) generally feature an additional gasoline tank used for cold starts when ambient temperatures are low [4].

A study on the evaporative properties of gasoline-bioethanol fuel blends was performed by using a simple thermodynamic model that considers gasoline an equivalent mixture of four ideal paraffins. Predicted enrichment coefficients required to ensure cold starts were compared to measured values for gasoline operation and several specific aspects of gasoline–ethanol fuel blends were investigated.

2 Thermodynamic Model
Pulverization and evaporation of gasoline resembles water evaporation, and so the idea for an $h-x$ (enthalpy – fuel mass participation) diagram was approached [5], similar to the Mollier diagram for humid air. While studies of fuel break-up and evaporation in compressions ignition [6] or SI direct injection engines [7] require complex models that employ computational fluid dynamics, a simple thermodynamic model can be used for port injection engines. The mixture was considered as a dry air and fuel vapor mixture, all being ideal gases at
relatively low pressure and high temperature, so that Dalton’s and Amagat’s laws can be used in calculations. As the liquid phase is far denser than gas, the volume of liquid fuel was considered insignificant. Air and liquid fuel before the evaporation process, as well as all engine components can be considered to have the same temperature, namely ambient temperature \(T_{amb}\), when the engine is cold. After the fuel evaporates, all components, air and fuel, reach the same temperature \(T_{mix}\). As a result air–fuel mixture temperature after fuel evaporation \(T_{mix}\) can be calculated using the energy balance equation, as during cold start practically no heat is transferred to and from engine components like the intake manifold, cylinder head and intake valve.

\[
T_{amb} - T_{mix} = \frac{x_v \cdot \frac{1}{\lambda \cdot AFR_{st}} \cdot \Delta h_{vap}}{c_{p,v} + \frac{1}{\lambda \cdot AFR_{st}} \cdot c_f},
\]

(1)

where \(T_{amb}\) and \(T_{mix}\) are measured in K, \(x_v\) is the fraction of evaporated fuel, calculated as the ratio \(m_v / m_l\), with \(m_v\) as the mass of vapor fuel and \(m_l\) total fuel mass, in kg, \(\lambda\) relative air–fuel ratio, \(AFR_{st}\) stoichiometric air–fuel ratio, \(\Delta h_{vap}\) fuel enthalpy of vaporization, measured in J/kg, \(c_{p,v}\) specific heat at constant pressure for air and \(c_f\) specific heat of liquid fuel, both measured in J/kgK.

Gasoline was considered a mixture of hexane, heptane, octane and decane, with proportions determined based upon the distillation curve [5]. Ethanol was considered as the fifth component of the blend. Therefore, \(\Delta h_{vap}\) for the fuel blend can be calculated using equation (2)

\[
\Delta h_{vap} = \sum_{i=1}^{5} \frac{x_{v_i} \cdot \Delta h_{vap,i}}{x_v},
\]

(2)

where \(x_v\) is the ratio of fuel vapor to air mass, calculated as \(m_v / m_{air}\), with subscript \(i\) denoting vapor mass and enthalpy of vaporization for component number \(i\).

LeChatelier’s rule was employed for calculating the lower flammability limit (LFL) for all fuel types

\[
LFL_{blend} = \frac{1}{\sum_{i=1}^{5} \frac{y_i}{LFL_i}},
\]

(3)

where \(LFL_{blend}\) is the LFL for the mixed fuels, \(y_i\) is the molar participation of component \(i\) of the blend and \(LFL_i\) is the LFL for component \(i\) [8]. It should be noted that using this equation resulted in a prediction of \(LFL = 0.998\%\) for gasoline, lower than the usual value of 1.4\%. However, given that this fuel was considered as an equivalent mixture of four components and evaporative properties were estimated using this assumption, the LFL value calculated using this method should be more relevant for this study.

Evaporated fuel ratio \(x_v\) was calculated using equation (4), with \(y_{vi} = \nu_i / \nu_v\) as the molar participation of component \(i\) in vapor fuel. It depends on the fuel vapor pressure \(p_v\), as the sum of partial pressures for every fuel component

\[
x_v = \frac{p_v}{p_{man} - p_v} \cdot \frac{1}{M_{air}} \cdot \sum_{i=1}^{5} y_{vi} \cdot M_i,
\]

(4)

where \(p_{man}\) is the intake manifold absolute pressure, with the same measurement unit as \(p_v\), \(M\) is the molar mass, measured in kg/mol, with subscript \(air\) denoting air and \(i\) for component \(i\) of the fuel blend.

Assuming equilibrium, with air and vapor as ideal gases, Raoult’s law combined with Dalton’s law gives equation (5), with \(y_i = \nu_i / \nu_v\) as the molar participation of component \(i\) in liquid fuel

\[
y_v = \frac{p_s}{p_v} \cdot \frac{y_i}{y_v},
\]

(5)

where \(p_s\) is the saturation pressure of component \(i\), with the same measurement unit as \(p_v\).

Defining the molar participation of component \(i\)

\[
y_i = \nu_i / \nu_v\]

as \(y_i = \nu_i / \nu_v\) (with \(\nu_i\) moles for component \(i\) and \(\nu_v\) moles for fuel), equations (6–8) can also be written, where \(y_v = \nu_v / \nu_v\) and \(y_i = \nu_i / \nu_v\) as the molar participations of vapor and liquid fuel

\[
y_i = y_{vi} \cdot y_i + y_{iv} \cdot y_v,
\]

(6)

\[
\sum_{i=1}^{5} y_{vi} = 1,
\]

(7)

\[
y_i + y_v = 1,
\]

(8)

while \(p_v\) and molar participations \(y_{vi}\) can be calculated using equations (5–9) solved by employing numerical methods for a given \(x_v\) as \(p_{vi}\) depends on \(T_{mix}\).
\[ x_f = \frac{p_v}{p - p_v} \cdot \frac{1}{M_{air}} \cdot \frac{1}{y_v} \cdot \sum_{i=1}^{n} y_i \cdot M_i, \quad (9) \]
with ratios \( x_{vi} \) and \( x_{li} \) calculated using equations (10) and (11)
\[ x_{vi} = \frac{p_v}{p_{man} - p_v} \cdot M_{i} \cdot y_v, \quad (10) \]
\[ x_{li} = \frac{p_v}{p_{man} - p_v} \cdot \frac{M_{i}}{M_{air}} \cdot \frac{y_i}{y_v}, \quad (11) \]
noting that equation \( \Sigma y_{vi} = 1 \) can also be written, but needs to be eliminated as the system is not determined.

3 Results and Discussion
A total of five cases were investigated, with pure gasoline and ethanol, as well as 10, 70 and 85% alcohol mixed with the fossil fuel. Studied volumetric concentration levels of 10 (E10), 70 (E70) and 85 % (E85) were chosen as 10 % is the upper limit of ethanol blended into gasoline that can be used in unmodified gasoline SI engines, with E85 as the usual blending rate for flex fuel vehicles (FEVs) and E70 the blend used in cold ambient temperature conditions.

Figures 1 and 2 present calculated mixture cooling (\( T_{amb} - T_{mix} \)) and evaporated fuel fraction \( (x_e) \) for gasoline and pure ethanol (E100) at stoichiometric air–fuel ratio. Given that ethanol features a much higher enthalpy of vaporization compared to gasoline, increased mixture cooling of up to 76 K is calculated for E100 compared to a maximum value of 20 K for gasoline.

Elevated enthalpy of vaporization, combined with a lower saturation pressure, also leads to much lower fraction of evaporated fuel when using E100. An interesting observation is that for stoichiometric air–fuel ratio, E100 is fully evaporated at air temperatures of over 380 K, while gasoline is fully evaporated at 340 K. The actual values are not that significant for real air–fuel mixture formation, but the 40 K difference is quite important. Measurements performed by the authors with a port injection engine warmed–up revealed that intake air is heated by 20–40 K at light load, while at full load very little air heating occurs. As injection usually takes place with the intake valve closed or partially open, additional heat is transferred from warm engine components to the air–fuel mixture through the fuel film in the intake port [9]. Given that heat transfer to the air–fuel mixture is optimized for gasoline in SI engines, it is highly probable that incomplete evaporation will occur when E100 is used, even with the engine warmed–up.

A very important property of any fuel is its LFL, as this value limits its use in SI engines. A mixture too lean will result in cold start failure and decreased engine performance due to higher cyclic variations, slow flame development and even incomplete combustion. Predicted air temperature limits for successful cold start with stoichiometric air–fuel mixtures are shown in figure 3 for gasoline and figure 4 for E100. An engine operated on gasoline will feature much better cold start performance in cold ambient conditions. It should be noted that a port injection engine using a stoichiometric air–gasoline mixture will start at much lower temperatures than the predicted limit of 292 K calculated using the simple thermodynamic model. This is due to a more complex air–fuel mixing process, involving a fuel film that is present in the intake port from the first injection events.

Fig.1 Calculated air–fuel mixture cooling and evaporated fuel fraction for E100

Fig.2 Calculated air–fuel mixture cooling and evaporated fuel fraction for gasoline
Another reason for the relatively high predicted cold start temperature limit is that the model most likely underpredicts the mass of fuel vapor in the mixture at low ambient temperatures. Gasoline contains components with a boiling temperature as low as 300 K, while hexane, the component with the lowest boiling temperature in the equivalent mixture used for calculations, has a boiling point of 342 K. Further investigation into the effect of the fuel film in the intake port, as well the influence of the equivalent mixture composition should provide a significant improvement into the prediction of the lower temperature threshold for reliable cold start performance of port injection SI engines.

An interesting application of the model is calculating required enrichment ratios (defined as the fuel–air ratio during engine cranking referenced to the fuel–air ratio during stoichiometric operation). Enrichment before the engine is started, is required mostly during winter, when the ambient air is too cold to ensure proper fuel evaporation. Therefore, enrichment ratios of up to 5 are employed at ambient temperatures below 280 K.

The model predicts a required enrichment coefficient of almost 30 so that cold start can be achieved at 290 K when using E100 (figure 5), while for gasoline hardly any enrichment would be necessary (figure 6).

![Fig.3 Calculated mass and volumetric evaporated fuel fraction, compared to the LFL of E100](image1)

![Fig.4 Calculated mass and volumetric evaporated fuel fraction, compared to the LFL of gasoline](image2)

![Fig.5 Evaporated fuel fraction for different enrichment ratios and air temperatures for E100](image3)

![Fig.6 Evaporated fuel fraction for different enrichment ratios and fuel blends at 287 K air temperature](image4)

![Fig.7 Evaporated fuel fraction for different enrichment ratios and fuel blends at 287 K air temperature](image5)
Again, the actual values are not that significant for real world operation, but the massive difference between the two fuels is obvious. The increased evaporative properties of gasoline compared to E100 are also evident when comparing different blending ratios of gasoline and ethanol (figure 7). By adding only 15% vol gasoline to ethanol, the required enrichment ratio is almost half (around 30 compared to almost 60) compared to E100 at 287 K. Adding more gasoline significantly improves the evaporative properties of the fuel blend, explaining why fuel handlers sell E70 labeled as E85 during winter. No significant difference was observed for E10.

![Graph](image1)

**Fig. 8** Engine operational parameters during a cold start at an ambient temperature of 287 K

An analysis of figure 8 reveals that the fuel system performs an initial enrichment ratio of up to 3.2. In the initial phase an injection time of over 20 ms was briefly employed by the electronic control unit (ECU), for a few rotations of the crank shaft. After the engine was started, the injection time dropped sharply down to 6 ms. After the engine's coolant temperature reached its nominal value of 360 K, the injection time was decreased to 2.6 ms and a stoichiometric air–fuel mixture was obtained. In order to calculate an enrichment coefficient, the variation in intake air density needs to be taken into account. Given that the injectors open once every rotation of the crank shaft, fuel flow is proportional to the injection time and engine speed. Therefore, air–fuel ratio will be determined by the injection time and intake air density, as air flow is proportional to engine speed. All parameters shown in figure 8 were recorded with the engine running at idle, with slight engine speed variations, around 900 rev/min. During the first phase, when cranking the engine, intake air density was high, as no air heating occurs. After the engine was started, absolute manifold pressure drop sharply, with values below half of ambient pressure. When the engine warmed–up, an additional decrease of intake air density was evident, given that air temperature was higher. Based on these observations, an enrichment factor was calculated (figure 9) for the recorded parameters shown in figure 8.

![Graph](image2)

**Fig. 9** Calculated enrichment coefficient for an ambient air temperature of 287 K

Table 1 also presents calculated air density for three main phases during engine cold start and the corresponding enrichment coefficient.

<table>
<thead>
<tr>
<th></th>
<th>Cranking</th>
<th>Immediately after engine start</th>
<th>Engine warm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air density [kg/m³]</td>
<td>1.214</td>
<td>0.722</td>
<td>0.475</td>
</tr>
<tr>
<td>Injection time [ms]</td>
<td>20.46</td>
<td>6.28</td>
<td>2.52</td>
</tr>
<tr>
<td>Enrichment coefficient [-]</td>
<td>3.177</td>
<td>1.639</td>
<td>1</td>
</tr>
</tbody>
</table>

**Table 1 Cold start air and fuel flow parameters**
Given that other studies using multi-component mixtures as an equivalent for gasoline found that the ideal liquid assumption does not significantly increase the error level [10], the reason most likely for the overprediction of the required enrichment factor is that the model does not predict the evaporative properties well enough in the low temperature range. While the thermodynamic model can predict with acceptable accuracy cold start gasoline–air mixture temperature cooling down to 260 K [3], a more precise description of the evaporative properties of this fuel needs to be achieved at low ambient temperatures.

Another issue is that short chain alcohols increase vapor pressure [11] as compared to higher alcohols such as isobutanol [12].

4 Conclusion
A simple thermodynamic model was used for investigating the evaporative properties of gasoline–bioethanol fuel blends.

A direct comparison of gasoline and ethanol was possible in order to evaluate how cold start performance is affected when using alcohols in port injection SI engines. The model correctly predicts a significant improvement of evaporative properties for gasoline–ethanol blends, when more fossil fuel is added.

Further investigation is required, as the model needs to be improved by adding lighter components to the equivalent composition of gasoline. In this way, a more precise prediction of evaporated fuel fraction would be possible at low temperatures. Also, a fuel film conductive heat exchange sub-model needs to be added, as the required enrichment factor is overpredicted even at high ambient temperatures.

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References: