

AIR-FUEL $h - x$ DIAGRAM FOR GASOLINE-ISOBUTANOL BLENDS

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Biofuels can significantly contribute to green house gas emissions reduction, as they are obtained from biomass. The use of alcohols for fuelling spark ignition (SI) engines raises an array of problems in the fields of fuel production, transport and other applications. Compared to ethanol or methanol, isobutanol has the advantage of much lower corrosion that can be a major problem for fuel systems built to run on gasoline only. An important aspect of alcohols used as fuel is their high latent heat of vaporization, making cold starts during winter very difficult. Therefore, the present paper proposes a method of investigating air-fuel mixture properties when fuelling SI engines with gasoline-isobutanol blends. Using the air-fuel enthalpy-mass participation ($h - x$) diagram, a final mixture temperature can be calculated, as well as the quantity of fuel that actually evaporates. Compared to previous work on the subject of $h - x$ diagrams for gasoline, a higher precision is ensured and new diagrams are plotted for concentrations of 30 %, 50 % and 70 % isobutanol mixed with gasoline, as well as a diagram for pure isobutanol.

Key words: Isobutanol, Spark ignition engines, Air-fuel mixture, $h - x$ diagram.

1. INTRODUCTION

As biodiesel has become the main biofuel for compression ignition (CI) engines, bioethanol seems to be the fuel most likely to be used as an alternative for spark ignition (SI) engines. However, given its advantages, biobutanol is a much better replacement as a drop-in fuel for SI engines. Biobutanol is a renewable energy source as it is obtained from biomass, and using it as a fuel produces less pollutant emissions.

Compared to ethanol, butanol is much less corrosive and is practically insoluble in water. This means that phase separation does not occur in gasoline-butanol blends and existing fuel distribution infrastructure can be used without modifications. Another great advantage is that butanol has a heating value ~ 25 % higher than that of ethanol [1], and given its lower oxygen content, butanol can be blended with gasoline in greater percentage than the 10 % limit imposed for ethanol when fuelling non-modified SI engines. Good results are reported for fuel blends with up to 30 % biobutanol mixed with gasoline [2, 3]. Also, compared to gasoline-ethanol blends, adding butanol to gasoline has a less significant effect on the fuel distillation curve [4], [5].

Isobutanol (IB) is an isomer of n-butanol, with the same molar mass of 74,122 kg/kmol, a boiling temperature of 107.65 °C [6] and carbon atoms arranged in a different manner than for n-butanol. IB has similar properties compared to n-butanol, with the great advantage of higher octane rating, close to the premium gasoline range [7]. Energy density is lower compared to gasoline, while the energy contained in stoichiometric air-fuel mixtures is very close for both fuels (table 1).

One important property of IB, as with all alcohols, is its high enthalpy of vaporization, higher than that of gasoline. This makes cold starts during winter very difficult. The study presented in this paper proposes enthalpy-fuel mass participation ($h - x$) diagrams that can be used for investigating air-fuel mixture properties in SI engines fuelled with gasoline-isobutanol blends. These diagrams show enthalpy (h) levels for air-fuel mixtures with different fuel mass participations (x) for a temperature range of -40 to 80 °C. Besides mixture temperature and fuel concentration, air-fuel mixture pressure greatly influences the dew point and saturation pressure of gasoline and IB. As intake manifold absolute pressure levels can range from 0.2 bar to 1 bar in naturally aspirated SI engines, three levels were chosen for the diagrams, with 0.2; 0.6 and 1 bar.

As the addition of IB to gasoline greatly influences evaporative properties of the fuel blend, air-fuel mixture properties need to be closely investigated so that good engine operation is achieved. Using the $h-x$ diagrams developed by the author, mixture temperature levels and evaporated fuel ratios can be calculated for a wide range of IB concentrations mixed with gasoline. In this way, maximum concentrations of IB can be identified for a given temperature range, so that good cold start characteristics are achieved. A positive aspect is that using IB increases engine volumetric efficiency due to lower mixture temperatures. Given its high oxygen content, however, IB in high concentrations mixed with gasoline can lead to a severe loss of power in unmodified SI engines. Even if part load operation is satisfactory up to 50 % IB mixed with gasoline, full load performance becomes erratic [8].

Table 1

Fuel properties [6, 7]

Fuel	Density [kg/l]	Energy density [MJ/l]	Stoichiometric mixture energy density [MJ/kg]	Stoichiometric air-fuel ratio [kg _{air} /kg _{fuel}]	Vaporization enthalpy at 20°C [kJ/kg]
Gasoline	0.72 – 0.78	30.2 – 33.95	2.67 – 2.81	14.7	360
IB30*	0.75 – 0.79	29.21 – 31.87	2.68 – 2.79	13.6	466
IB50*	0.77 – 0.80	28.55 – 30.48	2.69 – 2.77	12.9	533
IB70*	0.79 – 0.80	27.89 – 29.09	2.70 – 2.75	12.2	598
IB100*	0.81	26.9 – 27	2.72 – 2.73	11.2	690

* 30 %, 50 %, 70 % and 100 % isobutanol volumetric participation in the fuel blend with gasoline

2. AIR-FUEL $h-x$ DIAGRAM

Mixture formation in port fuel injection SI engines is a complex heat and mass exchange process between intake air and injected fuel, with droplet size being the most important factor. The fuel droplets gradually evaporate in contact with air, a process very similar to water evaporation. Thus, the idea of using an enthalpy-fuel mass participation $h-x$ diagram for air-fuel mixtures came about, like the Mollier diagram for humid air.

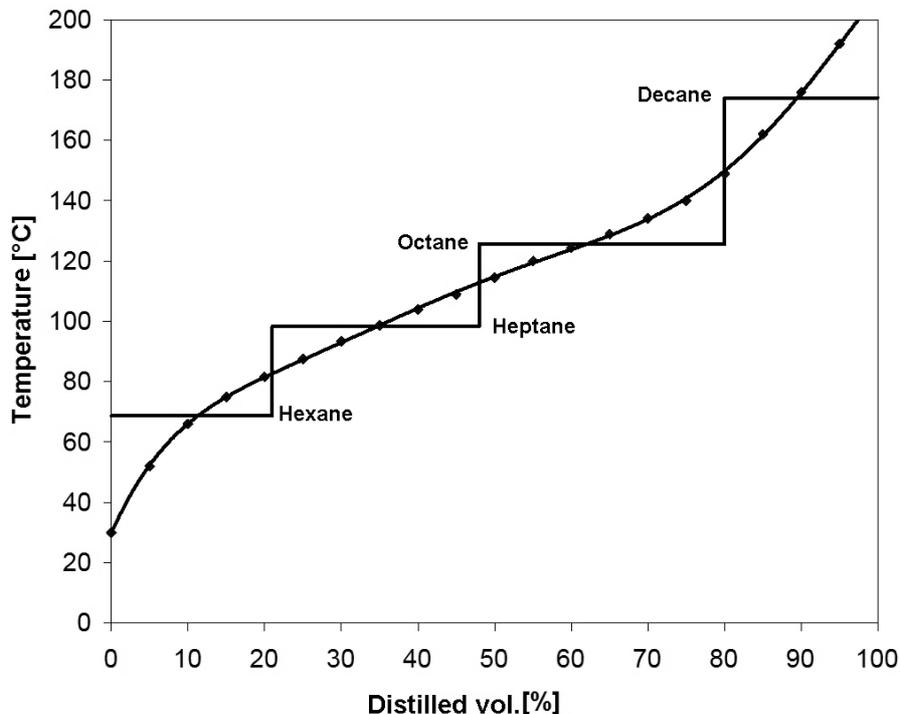


Fig. 1 – Distillation curve for gasoline and the equivalent mixture of hexane-heptane-octane-decane.

Several hypothesis were used when calculating air-fuel mixture enthalpy (h). Air and fuel vapour were considered ideal gases at relatively low pressure, so that Dalton's and Amagat's laws can be applied. Gasoline is a mixture of hydrocarbons with different boiling points at a given pressure level. When calculating enthalpy values for the $h - x$ diagram, gasoline was considered a mixture of four paraffin components, hexane (C_6H_{14}), heptane (C_7H_{16}), octane (C_8H_{18}) and decane ($C_{10}H_{22}$). Previous work conducted on the $h - x$ gasoline diagram considered the fuel as a mixture of three components (C_6H_{14} , C_7H_{16} , C_8H_{18}) [9], however, four components ensure a higher precision [10]. Molar participations (y_i) for the four components of the fuel mixture equivalent to gasoline were calculated based on the distillation curve (Fig. 1).

Equation (1) is the result of combining definitions of molar participations for component i of the fuel blend as $y_i = v_i / v$, with v_i moles for component i and v moles of fuel, and subscripts l and v standing for *liquid* and *vapour*. Therefore, $y_l = v_l / v$ is the molar participation of liquid fuel and $y_v = v_v / v$ the participation of fuel vapour, while $y_{li} = v_{li} / v_l$ and $y_{vi} = v_{vi} / v_v$ are the molar participations of component i in liquid and vapour state. Equations (2), (3) and (4) can also be written by combining these definitions.

Longer chain alcohols mixed with gasoline do not show high deviations from an ideal solution when evaporating, as methanol or ethanol do [11]. Therefore, equation (5) can be used, as the result of combining Dalton's and Roault's laws. Equations (1), (2), (3), (4) and (5) written for a fuel with n components, allow for molar participations to be calculated at every point of the $h - x$ diagram:

$$y_i = y_{li} \cdot y_l + y_{vi} \cdot y_v, \quad (1)$$

$$\sum_{i=1}^n y_{li} = 1, \quad (2)$$

$$\sum_{i=1}^n y_{vi} = 1, \quad (3)$$

$$y_l + y_v = 1, \quad (4)$$

$$y_{vi} = \frac{p_{s_i}}{p_v} \cdot y_{li}, \quad (5)$$

where y_i is the molar participation of component i , with l standing for *liquid* and v for *vapour*, p_{s_i} the saturation pressure for component i and p_v vapour pressure of the fuel vapour in the air-fuel mixture, both measured in Pa.

As the liquid phase is far denser than gas, the volume of liquid fuel was considered insignificant. Equation (6) can be written by combining the ideal gas equation of state with Dalton's law and defining fuel mass participation as $x_{vi} = m_{vi} / m_a$, with m_{vi} mass of fuel vapour and m_a air mass. After calculating y_{vi} , y_{li} and p_v , vapour (x_{vi}) and liquid (x_{li}) fuel mass participations can be found using equation (6) and (7):

$$x_{vi} = \frac{p_v}{p - p_v} \cdot \frac{M_i}{M_a} \cdot y_{vi}, \quad (6)$$

$$x_{li} = \frac{p_v}{p - p_v} \cdot \frac{M_i}{M_a} \cdot \frac{y_l}{y_v} \cdot y_{li}, \quad (7)$$

where x_{vi} and x_{li} are the vapour and liquid fuel mass participations in the air-fuel mixture, p is the absolute pressure of the mixture measured in Pa, M_i the molar mass of component i , and M_a molar mass of air, both measured in kg/kmol.

Finally, fuel enthalpy (h_f) can be calculated with equation (8), air enthalpy (h_a) with (9) and mixture enthalpy (h) is the result of adding the two, with equation (10):

$$h_f = t \cdot \left(\sum_{i=1}^n x_{v_i} \cdot c_{p_{v_i}} + \sum_{i=1}^n x_{l_i} \cdot c_{p_{l_i}} \right) + \sum_{i=1}^n x_{v_i} \cdot r_i, \quad (8)$$

$$h_a = c_{p_a} \cdot t, \quad (9)$$

$$h = h_a + h_f, \quad (10)$$

where h_f is the fuel enthalpy measured in J/kg, t is the mixture temperature in °C, c_p constant pressure heat capacity in J/(kg·K), r latent heat of vaporization in J/kg, h_a air enthalpy measured in J/kg and h air-fuel mixture enthalpy in J/kg.

It must be noted that h_f , h_a and h are not actual enthalpy values (or more correct, specific enthalpy), but rather relative values referenced to the specific enthalpy value at 0 °C. As this temperature is also used as a reference point in Mollier's h – x diagrams, the same method was used in the present work.

The diagram for air-gasoline mixtures is obtained (Fig. 2) by plotting enthalpy points calculated at dew point (constant pressure bolded lines) and at constant temperature.

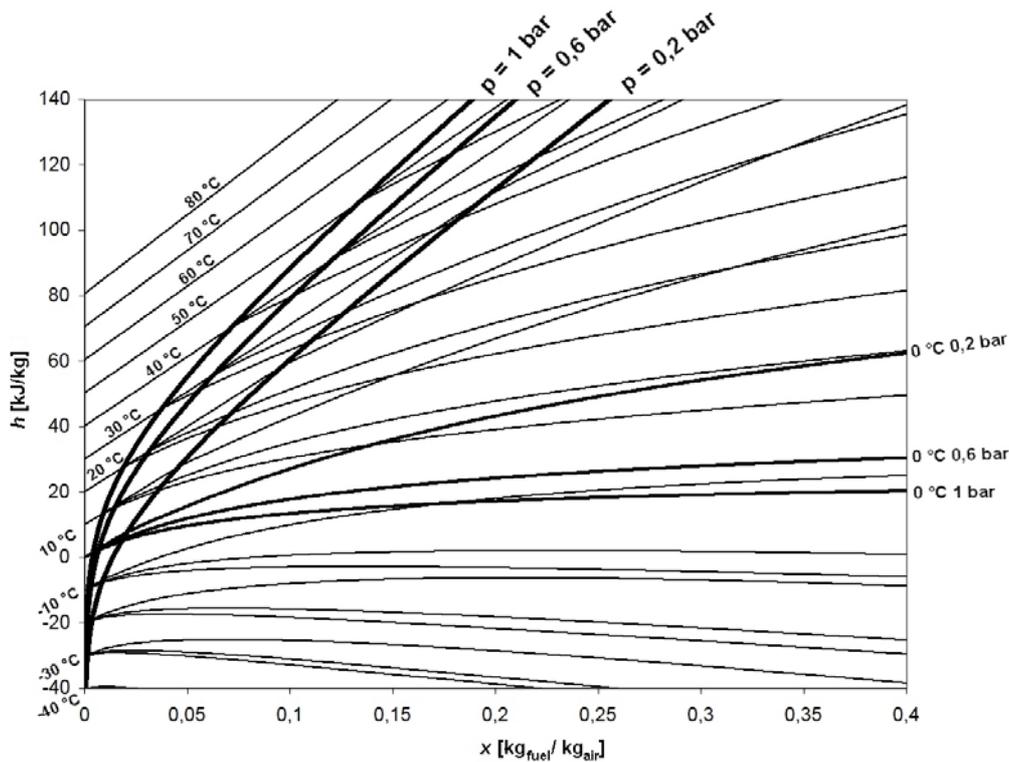


Fig. 2 – Gasoline air-fuel h – x diagram.

The diagram can be divided into two areas, the area above the *dew point line* (bolded lines in Fig. 2) and the one below. This division depends on absolute manifold pressure. At light loads manifold pressure shows lower values, as low as 0.2 bar at idle, while at full load operation the pressure in the intake port is close to 1 bar for naturally aspirated engines. The area above the *dew point line* contains air and fuel vapour. Below this division line, liquid components are also found, as the fuel does not completely evaporate. At high manifold pressure, the non-saturated domain (above the dew-point line, where the fuel is fully evaporated) is narrower than at low pressure values (Fig. 2). Therefore, a stoichiometric air-gasoline mixture ($\lambda = 1$ or $x = 0.068$) has a dew point of 39.05 °C at 1 bar manifold pressure, while at 0.2 bar pressure, the dew point is much lower, at 15.23 °C. This means that at high load, when the absolute manifold pressure is

also high, the air-fuel mixture needs to be at a temperature higher than 39.05 °C so that gasoline is fully evaporated. This is the reason why engine manufacturers intentionally heat the intake air and the fuel is injected directly onto the intake valve. Even if this lowers volumetric efficiency, completely evaporated fuel ensures low carbon monoxide (CO) and unburned hydrocarbons (HC) emissions.

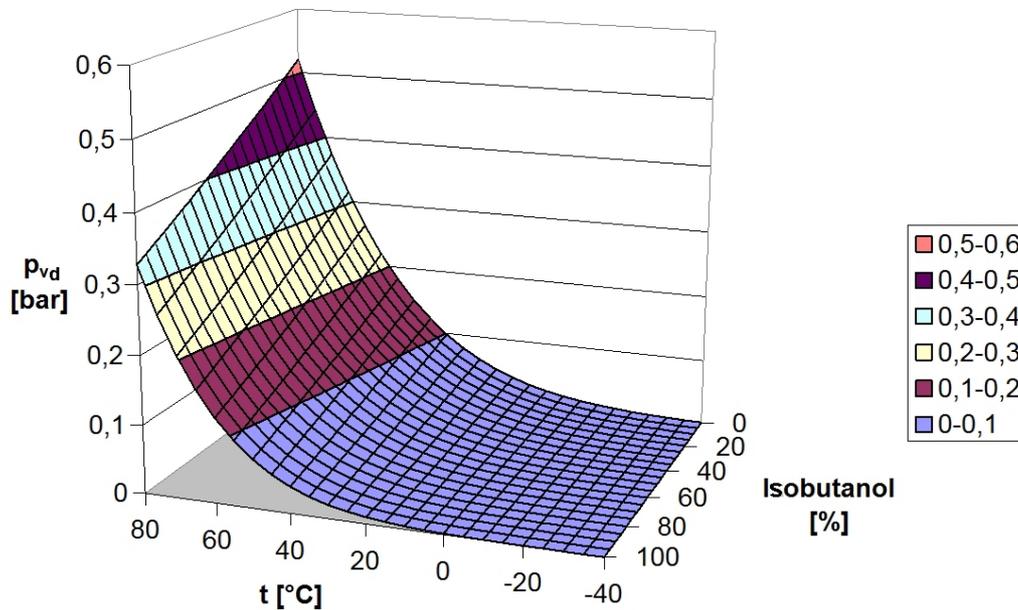


Fig. 3 – Dew point vapour pressure for gasoline-isobutanol blends.

Because IB has a low saturation pressure, gasoline-isobutanol blends have a lower dew point vapour pressure (p_{vd}) compared to pure gasoline (Fig. 3). This means that by adding IB to gasoline, cold start performance of the engine is practically limited more or less, as the fuel blend contains more or less alcohol.

Compared to the air-gasoline diagram (Fig. 2), gasoline-isobutanol fuel blends were considered mixtures of five components (hexane, heptane, octane, decane and IB), when calculating h values for IB30 (30 % IB with 70 % gasoline, Fig. 4), IB50 (50 % IB with 50 % gasoline, Fig. 5) and IB70 (70 % IB with 30 % gasoline, Fig. 6). Mixture enthalpy for IB30 is slightly higher than that for gasoline at the same temperature level (Figs. 2 and 4). Higher mixture enthalpy means lower air-fuel mixture temperature after the fuel is partially or fully evaporated.

An interesting observation is that *dew point lines* draw closer as the concentration of IB increases, while the non-saturated domain narrows. A narrow non-saturated domain means that less fuel can be evaporated when high concentrations of IB are mixed with gasoline. At 1 bar pressure and 29 °C mixture temperature, a saturated air-isobutanol mixture, with a fuel mass participation of $x = 3.07$ %, is just above the lower flammable limit of 3.03 % [12]. This is the reason why pure IB cannot be used for fuelling engines in regions where ambient temperatures drop below ~ 30 °C. Compared to ethanol that can be used for fuelling SI engines at relatively low ambient temperatures, down to ~ 12 °C, this is a major disadvantage. Experimental investigations conducted by the author identified IB50 as the maximum concentration of alcohol in gasoline-isobutanol blends, that insures good engine start-up characteristics even at temperatures around 0 °C. For higher concentrations of alcohol, such as IB70, the engine would stop right after it started or even did not start at all after numerous attempts. Because of its low saturation pressure, IB most likely causes the air-fuel mixture to be leaned out beyond the ignitable limit. Even though the injection system ensures a good break-up of the liquid, very little fuel vapour reaches inside the cylinder. After the engine starts, the electronic control unit gradually leans the very rich mixture needed for cold starts, and because of the high IB concentration in the fuel blend, there is too little gaseous fuel to ensure ignition. As a result, the engine stops after just a few seconds after it started, when fuelled with IB70.

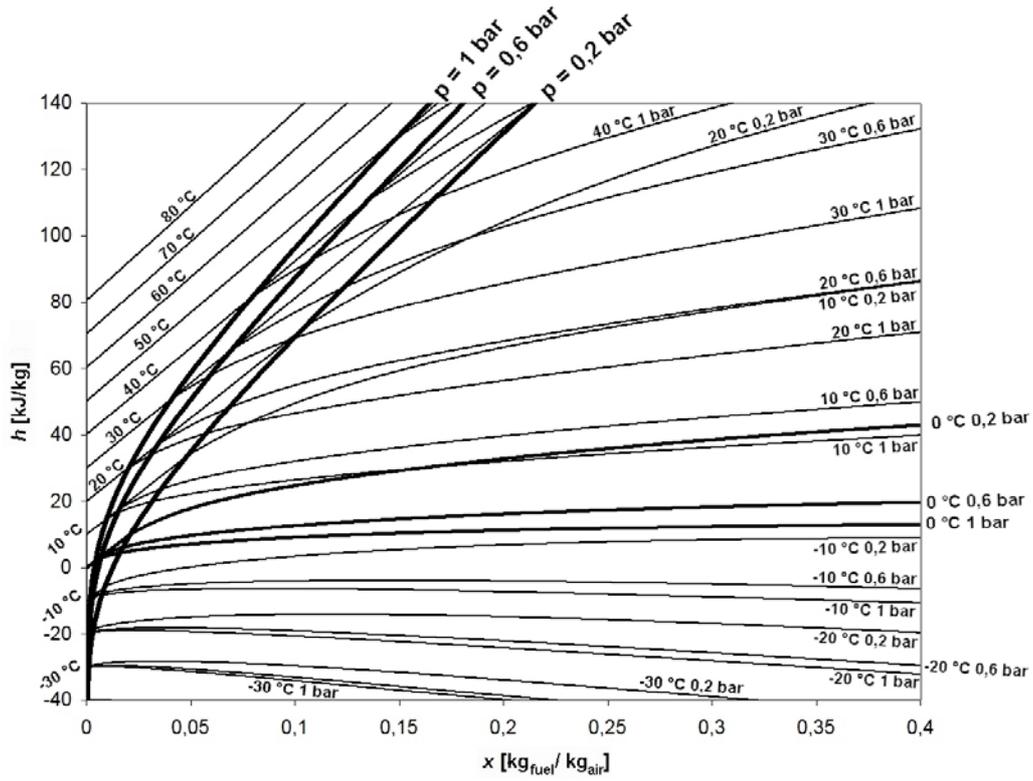


Fig. 4 – IB30 air-fuel $h - x$ diagram.

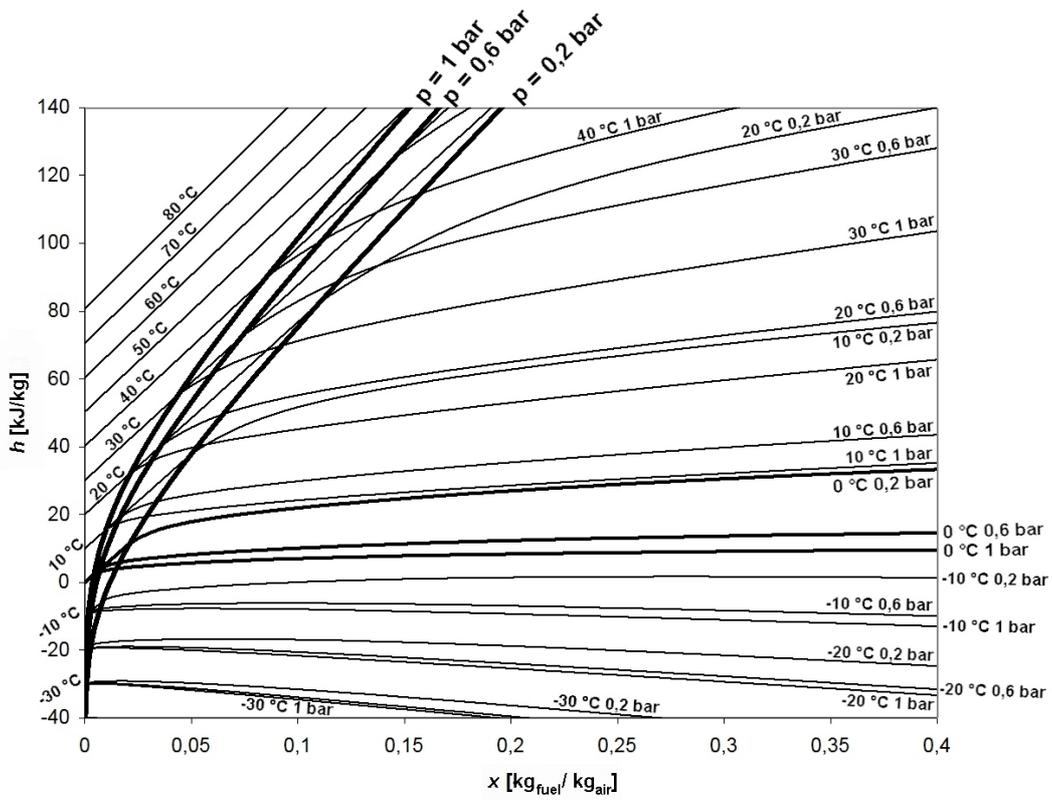


Fig. 5 – IB50 air-fuel $h - x$ diagram.

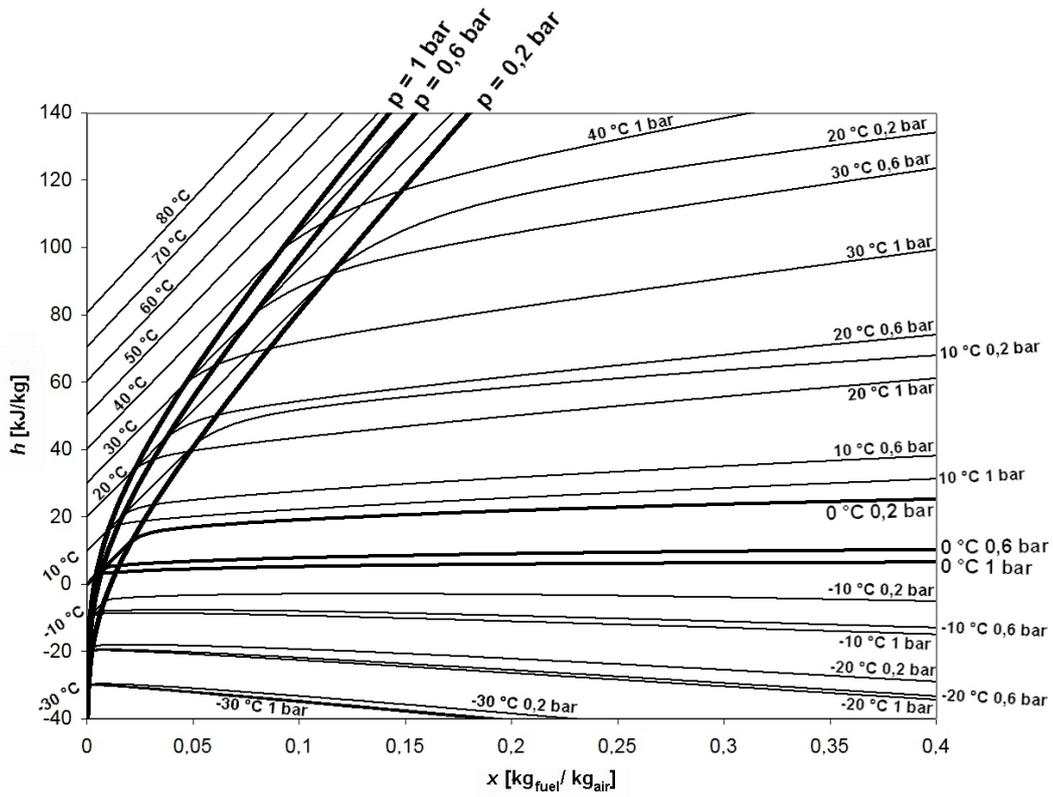


Fig. 6 – IB70 air-fuel $h - x$ diagram.

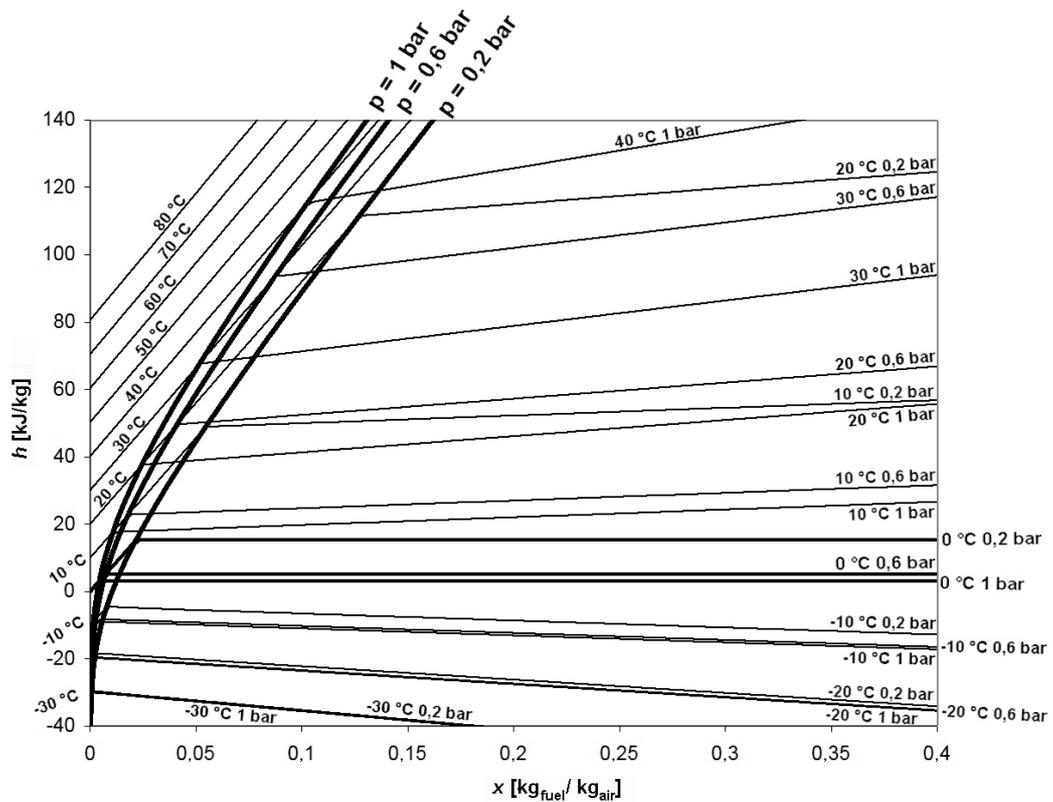


Fig. 7 – IB100 air-fuel $h - x$ diagram.

The $h - x$ diagram for pure isobutanol (IB100) has a very different shape than for the other blends (figure 7), with straight lines at constant temperature in the domain below the *dew point lines*. Mixture enthalpy increase in the saturated domain is given by the enthalpy of the liquid added and therefore the variation of enthalpy (h) is proportional to the fuel mass participation (x).

3. CONCLUSIONS

As isobutanol can be blended with gasoline in higher concentrations compared to ethanol, without engine modifications, its use in SI engines could see a significant increase. In the present study, enthalpy-fuel mass participation ($h - x$) diagrams were calculated and plotted for IB mixed with gasoline in different concentrations. In addition to this new undertaking in the field of air-fuel mixture studies, the precision of calculated values was increased by considering gasoline a mixture of four components, compared to previous work in which only three components were considered. This ensures a better prediction of gasoline's evaporative properties.

By using the $h - x$ diagram, minimum air temperature levels that ensure good engine start-up performance can be easily identified for different gasoline-isobutanol blends. The improvement of volumetric efficiency due to isobutanol's higher latent heat of vaporization can also be evaluated. Based on such studies, fuel injection management can be optimized to ensure the best engine performance in all working conditions.

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