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PERFORMANCE AND EMISSION CHARACTERISTICS OF PYRIDINE AND ISOBUTANOL ADDED GASOLINE-ETHANOL-WATER BLENDS IN A SINGLE CYLINDER SI GASOLINE ENGINE

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Abstract: The phase equilibria, engine performance and gas emissions of gasoline-ethanol-water blends with pyridine and isobutanol added for increased water tolerance, were investigated. It was observed that pyridine addition produced slightly higher ratios of ethanol and water in the stable fuel blend when compared to isobutanol, and the water ratio increased with the additive amount. Engine performances and combustion characteristics of the fuel blends were measured in a single cylinder, four-stroke, spark-ignition (SI) gasoline engine using different engine speeds and compared with the commercial gasoline. The best engine performance results were obtained from the HEP2 blend, consisting of 8.94% ethanol, 4.26% water and 4.21% pyridine. Using this fuel blend, engine torque increased by 8.3% at low speeds, engine effective power increased by %5 at high speeds while specific fuel consumption decreased by 14% at optimum engine speeds. Compared to the commercial gasoline blend, NOx, CO and HC emissions were found to be reduced by as much as %32, %17.9 and %45.9, respectively. Results showed that the fuel properties of pyridine and isobutanol added gasoline-ethanol-water blends were enhanced due to increased ethanol and water content and the HEP2 blend can be used in SI engines as an alternative to commercially available gasoline, with advantages of increased engine performance and reduced emission rates.
Keywords: Ethanol fuel, Hydrous ethanol, Gasoline additive, Pyridine, Isobutanol

PİRİDİN VE İZOBÜTANOL KATKILI BENZİN-ETANOL-SU KARIŞIMLARININ TEK SİLİNDİRLİ BENZİN MOTORUNDAKİ PERFORMANS VE EMİSYONLARININ İNCELENMESİ

Özet: Su toleransını artırmak amacıyla piridin ve izobütanol ile katkılandırılmış benzin-etanol-su yakıt karışımlarının faz dengesi, motor performansı ve gaz emisyonları incelenmiştir. İzobütanol ile kıyaslandığında, piridin katkısının daha yüksek oranda etanol ve su içeren kararlı yakıt karışımları oluşturduğu, katkı miktarının artırılması ile su oranının da arttığı görülmüştür. Yakıt karışımlarının motor performansı ve yanma karakteristikleri tek silindirli, dört zamanlı, buji ateşlemeli (SI) benzin motorunda, değişen motor hızlarında ölçülmüş ve ticari benzin ile karşılaştırılmıştır. En iyi motor performans sonuçları %8,94 etanol, %4,26 su ve %4,21 piridin içeren HEP2 karışımından elde edilmiştir. Söz konusu yakıt karışımı kullanılarak, düşük devirlerde motor torkunda %8,3 artış, yüksek devirlerde ise motor efektif gücünde %5 artış görülmüş, ayrıca optimum devirde özgül yakıt sarfiyatının %14 oranında azaldığı tespit edilmiştir. Ticari benzin karışımı ile kıyaslandığında, NOx, CO ve HC emisyonlarında sırasıyla %32, %17,9 ve %45,9'a varan oranlarda düşüş kaydedilmiştir. Elde edilen bulgular, piridin ve izobütanol katkılandırılmış benzin-etanol-su karışımlarında yakıt özelliklerinin artan etanol ve su oranına bağlı olarak iyileştiğini ve HEP2 karışımının buji ateşlemeli motorlarda daha yüksek motor performansı ve daha düşük emisyon oranı avantajı ile ticari benzin karışımlarına alternatif olarak kullanılabileceğini göstermektedir.
Anahtar Kelimeler: Etanollü yakıt, Sulu etanol, Benzin katkı maddesi, Piridin, Izobütanol

NOMENCLATURE

Symbols

λ	Air-fuel equivalence ratio
b_e	Specific fuel consumption [g/kWh]
C_f	Correction factor
M_c	Torque, corrected [Nm]
m_f	Fuel consumption rate [g/h]
n	Engine rotation speed [rpm]
P_d	Inlet dry air pressure [kPa]
P_e	Engine effective power [kW]
T_0	Ambient temperature [°C]

Abbreviations

BSFC	Brake-specific fuel consumption [g/kWh]
CO	Carbon monoxides
G1	Commercial gasoline reference fuel
HC	Hydrocarbons
HE	Hydrous ethanol
HEn	Hydrous ethanol gasoline blend, n is the blend number
HEIn	Isobutanol added hydrous ethanol gasoline blend, n is the blend number
HEPn	Pyridine added hydrous ethanol gasoline blend, n is the blend number
LHV	Lower heating value
NOx	Nitrogen oxides
PM	Particulate matter emissions
SFC	Specific fuel consumption [g/kWh]
SI	Spark-ignition
UHC	Unburned hydrocarbons

INTRODUCTION

There is growing demand for petroleum based fuels such as gasoline and fuel-oil, although obtained from irreversibly depleting sources. Moreover, combustion of these fuels produces carbon monoxide (CO), unburned hydrocarbons (UHCs), nitrogen oxides (NO_xs) and particulate matter (PMs) emissions which pose a serious threat to the environment and human health (Bergthorson, 2015; Martins, 2019). Therefore, ways to reduce the use of gasoline must be seriously taken into consideration for a sustainable energy policy. Several alternatives to the gasoline-powered engines have been proposed, including fuel cells, solar-photovoltaic cells, air-zinc batteries, plug-in hybrids and gas-electric hybrids. Despite the recent surge of interest in zero-emission, electrical power based technologies, the traditional internal combustion engine is still the dominant technology in transportation and seems to remain so for the next few decades, especially in developing countries. In this context, it is of crucial importance to develop alternative fuels for internal combustion engines, which would provide the demanded power in a more cost effective and environmental-friendly way.

Ethanol is a decent option as an alternative fuel for the internal combustion systems, which has already been in commercial use for a long time in different parts of the world (Awad, 2018). Ethanol can be produced from biomass in large quantities (Gnansounou, 2005). It can be mixed with gasoline in different ratios, creating fuel blends with similar properties to pure gasoline. Either in pure form or as a gasoline-ethanol blend, ethanol can be used in spark-ignition (SI) engines without requirement of any significant modification (Çelikten, 2015). One of the most important advantages of ethanol is that it has a higher octane number than gasoline, which can increase the performance of an internal engine.

For optimum operational parameters, namely the compression ratio, air/fuel ratio and ignition time, it is possible to obtain higher engine performance by ethanol based fuels than with gasoline (Bechtold, 1997; Thakur, 2017; Rao, 2020). It has been reported that ethanol-gasoline blends increase the brake-specific fuel consumption (BSFC), which is an important measure of the fuel efficiency (Eyidoğan, 2010). The ethanol-gasoline blends cause less soot formation compared to gasoline, according to Lemaire et al. (Lemaire, 2010). The ratio of the ethanol in the blend is also known to effect the engine performance. Higher ethanol ratios were reported to increase the heat value of the fuel and decrease the burning time in the combustion chamber (Bayraktar, 2005). Besides its beneficial effects on the engine performance, ethanol can also reduce the harmful emissions, depending on the blending ratio and engine operational parameters. Indeed, many studies in the literature reported that ethanol-gasoline blends have significantly lower CO, NOx and UHC emissions compared to gasoline (Wicker, 1999; Zhuang, 2013; Elfasakhany, 2015; Costagliola, 2016; Costa, 2020). It has been suggested that higher ethanol content in the fuel blends lead to lower emissions (Durbin, 2007; Clairotte, 2013). Due to these facts, many countries including United States, China, India and Brazil have set targets for the near future, to increase the ethanol or biofuel usage, typically by ratios varying between 10% and 20% (Suarez-Bertoa, 2015). Considering the growing emphasis on the renewable fuels, it is likely that the ethanol concentrations in the gasoline will increase in the future.

One of the drawbacks of using ethanol is the high cost associated with the production of anhydrous ethanol. Ethanol is primarily produced by distillation from biomass, and the end product typically comes with a water content of 5%. Further separation of ethanol and water causes an exponential rise in the cost because of the azeotropic properties of the solution. Even after the separation is achieved, anhydrous ethanol has a great tendency to absorb moisture, which can lead to difficulties with its storage and transport, adding further cost for use of anhydrous ethanol (Belincanta, 2016). To avoid these difficulties, hydrous ethanol (HE) containing gasoline blends were proposed as an alternative to anhydrous ethanol blends. Hydrous ethanol is much cheaper than anhydrous ethanol, due to skipping of the costly drying process after the distillation (Melo, 2012). Hydrous ethanol is used in Brazil, with up to 4.9% (vol/vol) water content.

Although ethanol can be homogeneously mixed with either gasoline or water, the ternary gasoline-ethanol-water system does not mix well in every ratios. These blends have a low stability even in the presence of small concentrations of water, and high water content often leads to hazy and separated phases. This fact makes the direct use of stable gasoline-ethanol-water blends as fuel in gasoline engines an interesting research topic. According to Shirazi et al., most of the physiochemical properties of low to midlevel hydrous ethanol blends, apart from viscosity and phase separation temperature, are not significantly different from those corresponding to the anhydrous blends (Shirazi, 2018).

In the literature, hydrous ethanol blends have been generally associated with increased engine performance and reduced emissions, thanks to improvements in compression ratio, flame speed and combustion efficiency (Rajan, 1983; Chen, 2010, Schifter, 2013, Venugopal, 2013). Deng et al. reported better thermal efficiency and significantly decreased CO and HC emissions by hydrous ethanol gasoline, while the torque and power values were comparable with those obtained by pure gasoline (Deng, 2018). It is possible to increase the water tolerance of gasoline-ethanol-water blends by using additives. Muzikova et al. studied the phase stability of petrol blends with ethanol and found that ethyl tert-butyl ether reduced the phase separation temperature for the gasoline-ethanol-water blends (Muzikova, 2009). Nour et al. reported that pentanol and octanol addition to hydrous ethanol/diesel blend provides a better mixing stability with enhanced engine performance (Nour, 2019). Kyriakides et al. showed that oxygen rich molecules, such as ethyl tert-butyl ether, tertiary amyl methyl ether and palmitic promote water tolerance in the ethanol-gasoline blends, leading to reduced NO_x emissions (Kyriakides, 2013). In the same study, it was reported that use of gasoline containing 40% ethanol and 40% ethanol-water did not require a modification in the engine for an efficient combustion.

There is still a need for further research on the stability, performance and emission characteristics of gasoline-ethanol-water blends with different compositions. This study concerns the SI engine performances and emission characteristics of gasoline-ethanol-water blends with increased ethanol and water content through the use of isobutanol and pyridine as additives. Pyridine is highly hydrophylic and readily soluble in gasoline, ethanol and water. Isobutanol has a poor solubility in water, but a good solvent for organic molecules and may increase the inter-solubility of ethanol containing systems (Liu, 2016). Blends were subjected to performance tests in a single cylinder engine test bed. Engine performances, specific fuel consumptions and the emissions were measured and compared to those obtained with commercial gasoline.

EXPERIMENTAL

Preparation of Fuel Blends and the Effect of Additives on Phase Equilibria

Since the triple phase properties of gasoline-ethanol-water blend may vary with different labels of gasoline, seven blends with different gasoline/ethanol/water ratios were prepared to see the stability of ethanol and water in the gasoline without use of any additives. The gasoline ratios in the blends varied between 35% and 95% (Table 1). Blends were denominated as HEn, where HE stood for hydrous ethanol and n for the blend sample number. A certified commercial gasoline blend (95 octane) was used as the reference fuel. The reference fuel itself contains up to 5% ethanol. Anhydrous ethanol was obtained from Sigma-Aldrich in 99.9% purity. The blends were mechanically stirred and taken to a separating funnel after allowing enough time for any phase separation to occur. Then, the separated phases were distilled in a three-neck round bottom flask to determine the ratios of ethanol and water in the gasoline-rich phase.

To see the effect of pyridine and isobutanol, four different fuel blends were prepared in different additive ratios (Table 2). In all four blends, ethanol and water ratios were set to 10% and 5%, respectively. Blends were denominated as HEP and HEI, with P and I standing for pyridine and isobutanol, respectively. Pyridine (99.8%, anhydrous) and isobutanol (99%) were obtained from Sigma Aldrich. Physical properties of gasoline, ethanol, isobutanol and pyridine are summarized in Table 3. The ethanol, water and additive ratios in equilibrium with gasoline were measured using the same method as in the gasoline-ethanol-water blends, with the only exception that the distillation was conducted at 80 °C and 100 °C.

Table 1. Gasoline-ethanol-water blending ratios

Blend	Gasoline, %	Anhydrous ethanol, %	Water, %
HE1	95	5	0
HE2	85	10	5
HE3	75	15	10
HE4	65	20	15
HE5	55	25	20
HE6	45	30	25
HE7	35	35	30

Table 2. Gasoline-ethanol-water-additive blending ratios

Blend	Gasoline (%)	Ethanol %99.9 (%)	Water (%)	Pyridine (%)
HEP1	82.5	10	5	2.5
HEP2	80	10	5	5
Blend	Gasoline (%)	Ethanol %99.9 (%)	Water (%)	Isobutanol (%)
HEI1	82.5	10	5	2.5
HEI2	80	10	5	5

Table 3. Physical properties of ethanol, isobotanol and pyridine (Arning, 2009; Elfasakhany, 2018; İnternet-1; İnternet-2; İnternet-3).

Physical property	Gasoline	Ethanol	Isobutanol	Pyridine
Formula	C_8H_{15}	C_2H_5OH	$C_4H_{10}O$	C_5H_5N
Boiling point, °C	25-210	78.24	107.8	115.2
Density, kg/m^3	720-775	789.3	801.8	982.7
Vapor Pressure, mmHg	337-675	59.3	10.4	20.8
Solubility in water, ml/100 ml H_2O	<0.1	Miscible	10.6	Miscible
LHV, MJ/kg	43.5	27.0	33.3	34.1

Engine Performance and Emission Tests

Fuel blends were subjected to engine performance tests to measure the engine torques, engine effective powers and specific fuel consumptions. Measurements were conducted in engine speeds varying between 1600-3200 rpm, representing a typical operating range for a common automobile. All tests were performed in a Cussons P8160 single cylinder, four stroke, water cooling spark ignition (SI) gasoline engine equipped with a dynamometer (Fig.1). All tests were conducted in 6.4:1 compression ratio with full stoichiometric air-fuel equivalence ratio and engine load. For each test, the engine spark advance was adjusted to give the maximum torque. Other technical parameters of the engine are given in Table 4. The engine speeds and air/fuel ratios were controlled by a control panel. Engine torque and fuel consumption data were recorded after the engine reached steady state for the corresponding engine speed. Engine torque data were temperature and pressure corrected according to Eq. (1) (SAE, 2004). Engine effective power and specific fuel consumption were calculated from corrected torque values using Eq. (2). Specific fuel consumption values were calculated using Eq. (3).

$$C_f = \left(\frac{99}{P_d}\right)\left(\frac{T_0 + 273}{298}\right)^{0.5} \quad (1)$$

$$P_e = \frac{M_c n}{9549} \quad (2)$$

$$b_e = \frac{m_f}{P_e} \quad (3)$$

NO_x, CO and HC emissions in the exhaust gas were analyzed using a Sun MGA 1500S model infrared-type exhaust analyzer. Technical specifications of the exhaust analyzer are also given in Table 5.

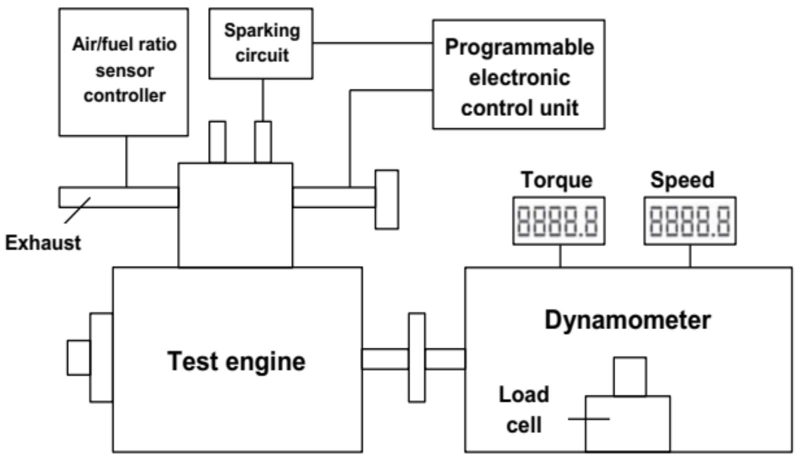

Figure 1. Schematic illustration of the experimental setup

Table 4. Technical parameters of the Cussons P8160 engine

Model	Cussons P8160
Number of cylinders	1
Maximum rotation torque	30 Nm
Maximum power	7.35 kW
Diameter x Stroke (mm)	77.79 x 82.55
Compression ratio	6.4:1
Fuel system	Injection

Table 5. Technical specifications of Sun MGA 1500S exhaust analyzer

Parameter	Measurement Range	Sensitivity
λ	0-15	0.001%
CO	0-14%	0.001%
NO_X	0-50000 ppm	1
HC (ppm)	0-9999 ppm	1
CO_2 (% vol.)	0-19%	0.01%
O_2 (% vol.)	0-25%	0.01%

RESULTS AND DISCUSSION

Phase Equilibria in Fuel Blends

The stability of gasoline-ethanol-water blends depends on the amount of water added and the properties of gasoline. For all mixing ratios containing water, phase separation occurred. The exception was HE1 blend containing 5% ethanol and 95% gasoline, in which all of ethanol was mixed in the blend. For other blends, the volumetric ratios of ethanol in the stable (gasoline-rich) phases to the total ethanol volumes were measured after phase separation (Fig. 2). It was clearly seen that the amount of ethanol passing to the stable phase decreased with the increasing water addition, because of the formation of strong hydrogen bonds between water and ethanol. These hydrogen bonds create the separate ethanol-water rich bottom phase which increases in volume with the water addition. The optimum mixing ratio was determined to be 85% gasoline, 10% ethanol and 5% water (HE2) which was to be taken as basis to study the effect of pyridine and isobutanol addition. For this mixing ratio, 50% of initial ethanol passed to the gasoline rich phase, producing a stable blend with 5.9% ethanol content.

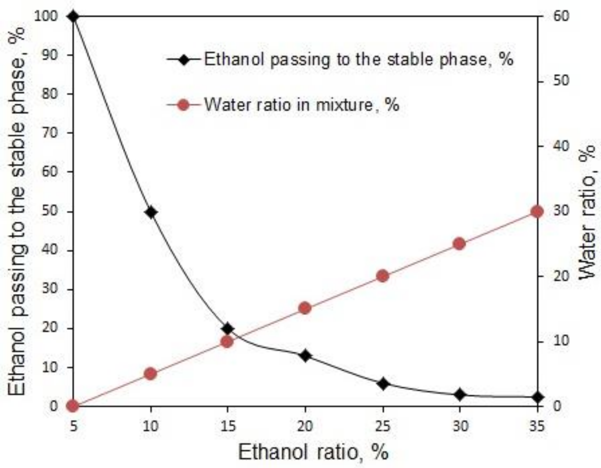

Figure 2. Percentage of ethanol passing to the stable gasoline-rich phase

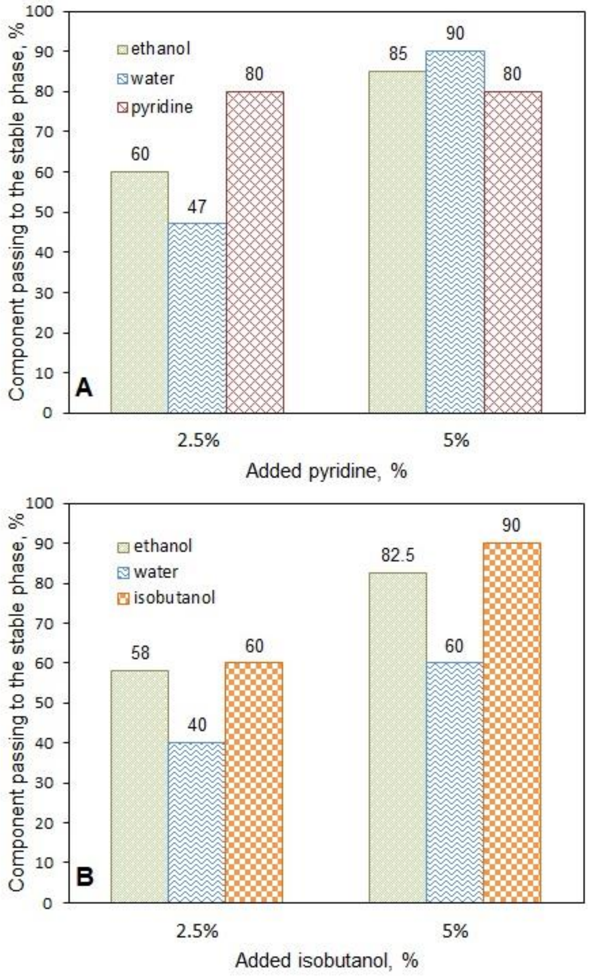

Figure 3. A) Percentages of ethanol, water and pyridine passing to the gasoline-rich phase B) Percentages of ethanol, water and isobutanol passing to the gasoline-rich phase

Table 6. Ratios of ethanol, water and pyridine/isobutanol in top (gasoline-rich) and bottom phases

Fuel Blend	Volume (ml)	Gasoline rich top phase (ml)	Bottom phase (ml)	Ethanol in top phase		Water in top phase		Pyridine / Isobutanol in top phase	
				ml	%	ml	%	ml	%
HEP1	194	180	14	12	6.67	4.7	2.61	4	2.22
HEP2	196	190	6	17	8.94	9	4.26	8	4.21
HEI1	196	179	17	11.5	6.42	4	2.23	3	1.68
HEI2	196	187	9	16.5	8.82	6	3.21	9	4.81

After addition of 2.5% pyridine to the HE2 blend, 60% of ethanol and 47% of water passed to the gasoline-rich stable phase (Fig. 3A). When the ratio of pyridine was increased to 5% (HEP2), the ratios of ethanol and water passing to the gasoline rich phase increased to 85% and 90%, respectively. HEP2 blend produced a stable fuel consisting of 82.6% gasoline, 8.94% ethanol, 4.26% water and 4.21% pyridine (Table 6). After addition of 2.5% isobutanol, 58% of ethanol and 40% of water passed to the gasoline-rich phase (Fig. 3B).

After the isobutanol ratio was increased to 5% (HEI2), these ratios increased to 82.5% and 60% for ethanol and water, respectively, producing a stable fuel solution of 79.2% gasoline, 8.82% ethanol, 3.21% water and 4.81% isobutanol. Overall, results show that pyridine addition is leading to slightly higher ratios of ethanol and water in the stable blend. The stronger hydrogen bonds forming between pyridine and water molecules may account for the increased ratio of water in the gasoline. On the other side, isobutanol molecules consist of a polar hydroxyl group which is hydrophilic, and a nonpolar alkyl group which is hydrophobic in nature. Isobutanol also increases the stable water content by acting as a cosolvent between the nonpolar hydrocarbon molecules and the polar water molecules.

Engine Performance

The gasoline-ethanol-water blends prepared by addition of different amounts of pyridine and isobutanol were subjected to engine performance tests and results were compared to those obtained from the commercial gasoline blend, which was denoted as G1.

Variation of the engine torques for different fuel blends at different engine speeds is given in Fig. 4A. At full engine load, the highest engine torques were obtained at 2400 rpm for each blend. The blends containing ethanol and water generally performed better than commercial gasoline, while the best results were obtained from the blends with higher additive ratios (5% pyridine or isobutanol). Results show that the performance was significantly improved by ethanol, while the presence of stable water did not cause any deterioration even at high ratios. At the optimum engine speed, the maximum engine torque was obtained as 21.3 Nm from the HEP2 blend, which is 3% higher than that obtained from G1 (20.7 Nm). The gap between HEP2 and G1 is even higher at low engine speeds (8.3% for 1400 rpm) and high engine speeds (4.4% for 3200 rpm). Low engine torques at low speeds are often associated with high rates of heat loss, where the compressed air/fuel loses a greater portion of its heat energy to the environment before ignition can occur. Considering that other possible factors such as valve leakages and ignition timing are equally affecting the blends, it can be deduced that the higher ethanol and water content in the blends increases the performance via reducing the heat losses at lower engine speeds. Another cause for low torque may be poor homogeneity due to low turbulence, which is often the case for low speeds. The fact that HEP2 gives higher performance than G1 at low engine speed shows that the blend is well mixed even at low turbulence.

On the other side, the engine effective power values are very close for all blends, except for those obtained at 3200 rpm (Fig. 4B). The HEP2 blend gave the highest effective power, which is 5% higher than G1 blend at the highest engine speed. The difference in effective power diminishes at lower engine speeds. The increased effective power in HEP2 and HEI2 blends can be explained by the improved combustion efficiency due to presence of hydrous ethanol. Yüksel et al. similarly reported that the ethanol-gasoline blends have higher effective power values compared to gasoline, especially at higher engine speeds (Yüksel, 2004).

The improved performance can be explained by increased octane number of the fuel due to increased hydrous ethanol content thanks to the additives. This results in a more advanced spark timing and increased knock resistance (Lanzanova, 2013; El-Faroug, 2016). Isobutanol also has a considerably high octane number, which is an additional contribution to the overall octane number of the blend (Allerman, 2020). Pyridine however, possibly has a greater effect on octane number by providing a higher hydrous ethanol ratio in the stable blend. Olberding et al., attributed the improvement of brake thermal efficiency in ethanol-water blend to reduced heat transfer losses due to lower burned gas temperature (Olberding, 2005). It is also reported that the increased amount of H, O and OH radicals resulting from dissociation of water can enhance the combustion (Zhang, 2012).

In terms of specific fuel consumption (SFC), the effect of increased ethanol and water ratio was more pronounced, as all gasoline-ethanol-water blends had

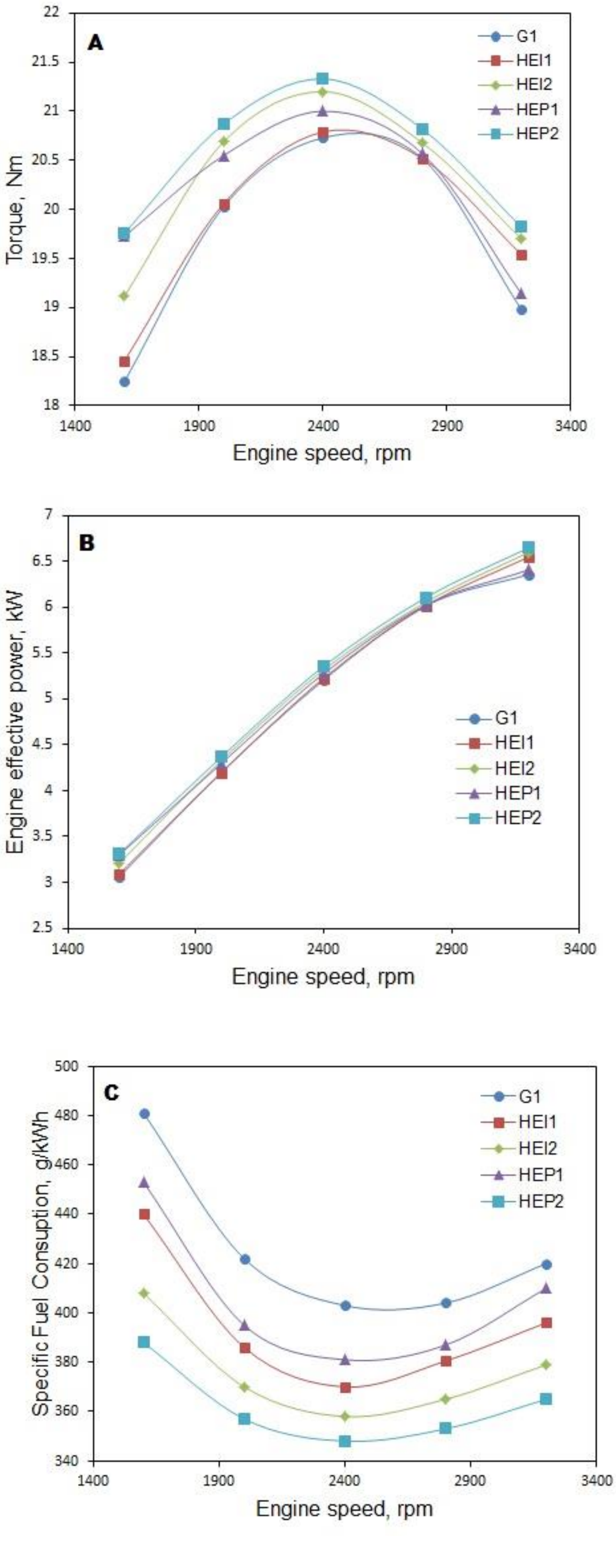

Figure 4. Variations of the torque (A), engine effective power (B) and specific fuel consumption (C) by the engine speed.

significantly lower fuel consumptions than the commercial gasoline blend (Fig. 4C). HEP2 and HEI2 blends containing the highest ethanol contents, gave the lowest fuel consumption values at the optimum engine speed of 2400 rpm with 347 g/kWh and 358 g/kWh, respectively. Those values are 14% and 11% lower than that of G1 blend, respectively. The increased ethanol content is thought to be the main contributing factor to the lower specific fuel consumption. Melo et al., reported an increase in SFC with hydrous ethanol, which they attributed to the lower heating value of hydrous ethanol (Melo, 2012). Ambros et al., however, found that increasing the water ratio in the ethanol led to an increase in the in-cylinder pressure and a decrease in the SFC (Ambros, 2015). Lanzanova also reported a decreased brake specific fuel consumption, which was attributed to the improved spark advance due to increased water content (Lanzanova, 2013).

NOx, CO and HC Emissions

The variation of the NOx emissions by the engine speed for different fuel blends is shown in Fig. 5A. The commercial gasoline blend has the highest NO_x emission concentration among all blends. The 5% pyridine added blend (HEP2) has the lowest amount of emission, in spite of the presence of N containing pyridine. It has been reported that, higher temperatures promote the formation of NO and N_2, in oxy-fuel combustion of pyridine, with the conversion ratios depending on the oxygen concentration (Wang, 2012). Therefore, the contribution of pyridine in the fuel seem to be less pronounced in total NO_x formation, compared to the reaction between air nitrogen and oxygen containing hydrocarbons. In general, higher cylinder temperature is known to facilitate NO_x formation, and the cylinder temperature increases with the engine speed, due to reduced heat transfer rate (Koç, 2009). The lower NO_x emissions on the side of ethanol-water blends may be due to lower in-cylinder temperature, as hydrous ethanol – gasoline (specifically, 10% ethanol) reportedly gives higher peak in-cylinder pressures and peak heat release rates compared to ethanol-gasoline (Wang, 2015). According to Lin et al., the high molar heat capacity and high heat absorption during vaporization may be effective in minimizing the peak flame temperature and reducing the NO_x formation rate (Lin, 2004). According to Fig. 5A, the difference in NO_x emissions is more pronounced at low engine speeds, where the NO_x emissions in HEP2 blend are 32% lower than that of commercial gasoline. Due to its limited heat absorbing capacity, water has a diminished effect at higher cylinder temperatures as evidenced by decreasing of NO_x emission differences at high speeds.

Variation of CO emissions with the engine speed can be seen in Fig. 5B. It is well known that the CO emissions are mainly due to insufficient oxygen concentration needed for a complete combustion. CO emissions seem to be slightly lower at optimal engine speeds (around 2400-2600 rpm) thanks to an increased amount of air intake and increased oxygen concentration in the cylinder. The lowest CO emission is obtained from HEP2 blend at 2400 rpm with 1.25%, which is 17.9% lower than that produced by commercial G1 fuel. At high engine speeds (3200 rpm), the CO emissions are increased due to reduced air intake. At this speed, CO emissions from HEP2 blend are still lower by 9.54% compared to G1 blend. Similarly in literature, the ethanol-gasoline blends are reported to reduce CO emissions (Li, 2015). Hydrous ethanol (10% ethanol) is also reported to produce slightly less CO emissions at low to medium load conditions (Wang, 2015). Water presence in the blend may decrease the CO emissions by way of altering the water-gas shift mechanism.

HC emissions are primarily resulting from incomplete burning of fuel, as in CO emissions. However, HC emissions are associated with low cylinder temperatures rather than low oxygen levels. To some degree, escaping fuel is another factor. In Fig. 5C, it can be seen that HC emissions decrease with engine speed due to increased temperature, even at low oxygen concentrations at high speeds. The increased CO emissions and reduced HC emissions at high speeds mainly result from the partial oxidation of HCs to CO at high temperature and low oxygen concentrations. The best results for HC emissions were again obtained from the HEP2 blend, whose HC emission is 21.9% lower than that of G1 fuel at 1600 rpm. The HC emissions are further reduced by 45.9% at 3200 rpm. This significant difference is due to several factors including higher heating value of ethanol, higher oxygen content and reduced heat transfer losses. Luo et al. similarly showed that hydrous ethanol blends decrease the HC emissions (Luo, 2017). Apart from the role of ethanol, water may also contribute to enhanced hydrocarbon combustion, because of the thermal dissociation of water molecules to produce free radicals.

CONCLUSIONS

Pyridine and isobutanol were used as additives to prepare gasoline-ethanol-water blends with increased ethanol and water ratios. Pyridine addition gave slightly higher ratios of stable ethanol and water compared to those obtained by isobutanol. In all blends, ethanol ratios varied between 6.42% and 8.94%, while water ratios varied between 2.23% and 4.26%. The best engine performance were obtained by the HEP2 blend, consisting of 8.94% ethanol, 4.26% water and 4.21% pyridine. Use of this blend significantly increased the engine torque and reduced the specific fuel consumption, while the engine effective power was not considerably affected, compared to commercial gasoline blend. The HEP2 blend also produced significantly lower NOx, CO and HC emissions, with reductions up to 32%, 17.9% and 45.9% respectively, at optimal operating conditions. The isobutanol added HEI2 blend also performed better than commercial gasoline, in terms of engine performance and emissions. Considering the favorable results obtained by higher ethanol and water ratios, the effect of pyridine and isobutanol seem to be due to increasing the aforementioned components ratios rather than being directly involved in the combustion process. It can be concluded that HEP2 and HEI2 blends can be used as alternative fuels in place of commercially available gasoline.

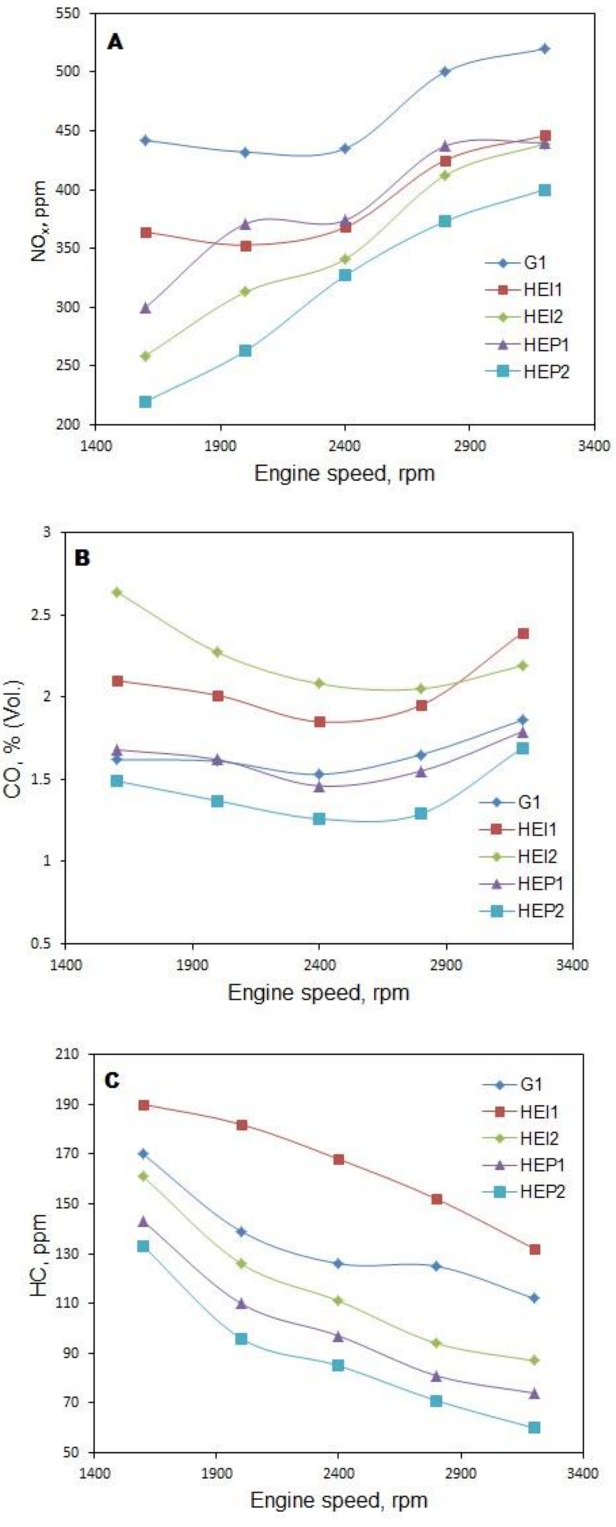

Figure 5. Variations of the NOx emissions (A), CO emissions (B) and HC emissions (C) by the engine speed.

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REFERENCES

Alleman T. L., Singh A., Christensen E. D., Simmons E. and Johnston G., 2020, Octane Modeling of Isobutanol Blending into Gasoline, *Energy Fuels*, 34(7), 8424–8431.

Ambros W., Lanzanova T., Fagundez J., Sari R., Pinheiro D. Martins M. and Salau N., 2015, Experimental Analysis and Modeling of Internal Combustion Engine Operating with Wet Ethanol, *Fuel*, 158, 270-278.

Arning J.,P., Peters W., Rieger B., Schmidt T., Schopf N. and Sternberg J., 2009, *Saacke Combustion and Energy Systems Pocket Formula Guide*, Saacke GmbH, Bremen.

Awad O.I., Mamat R., M. Ali O., Sidik N.A.C., Yusaf T., Kadirgama K. and Kettner M., 2018, Alcohol and Ether as Alternative Fuels in Spark Ignition Engine: A Review, *Renew. Sust. Energ. Rev.*, 82, 2586-2605.

Bayraktar H., 2005, Experimental and Theoretical Investigation of Using Gasoline Ethanol Blends in Spark Ignition Engines. *Renew. Energy*, 30(11), 1733-1747.

Bechtold R.L., 1997, *Alternative Fuels Guidebook*, Society of Automotive Engineers Inc., pp. 47-56.

Belincanta J., Alchorne J.A. and da Silva M.T., 2016, The Brazilian Experience with Ethanol Fuel: Aspects of Production, Use, Quality and Distribution Logistics, *Braz. J. of Chem. Eng.*, 33(4), 1091-1102.

Bergthorson J.M. and Thomson, M.J., 2015, A Review of the Combustion and Emissions Properties of Advanced Transportation Biofuels and Their Impact on Existing and Future Engines. *Renew. Sust. Energ. Rev.*, 42, 1393-1417.

Chen R.H., Chiang L.B., Wu M.H. and Lin T.H., 2010, Gasoline Displacement and NO_x Reduction in an SI Engine by Aqueous Alcohol Injection. *Fuel*, 89 (3), 604-610.

Clairotte M., Adam T.W., Zardini A.A., Manfredi U., Martini G., Krasenbrink A., et al., 2013, Effects of Low Temperature on the Cold Start Gaseous Emissions from Light Duty Vehicles Fuelled by Ethanol-Blended Gasoline. *Appl. Energy*, 102:44–54.

Costa R.C. and Sodré J.R., 2010, Hydrous Ethanol vs. Gasoline-Ethanol Blend: Engine Performance and Emissions. *Fuel*, 89(2), 287–293.

Costagliola M.A., Prati M.V., Florio S., Scorletti P. and Terna D., 2016, Iodice P., Buono D. and Senatore, A. Performances and Emissions of a 4-Stroke Motorcycle Fuelled with Ethanol/Gasoline Blends. *Fuel*, 183, 470–477.

Çelikten İ., Karaaslan E., Solmaz H., Okur M. and Polat S., 2015, Experimental Investigation of the Effects of Gasoline Additives on Engine Performance and Exhaust Emissions. *J. Therm. Sci. Tech.*, 35(1), 87-95.

Deng X., Chen Z., Wang X., Zhen H. and Xie R., 2018, Exhaust Noise, Performance and Emission Characteristics of Spark Ignition Engine Fuelled with Pure Gasoline and Hydrous Ethanol Gasoline Blends, *Case Stud. Therm. Eng*., 12, 55-63.

Durbin T.D, Miller J.W., Younglove T., Huai T. and Cocker K., 2007, Effects of Fuel Ethanol Content and Volatility on Regulated and Unregulated Exhaust Emissions for the Latest Technology Gasoline Vehicles. *Environ. Sci. Technol.*, 41:4059–64.

El-Faroug M.O, Yan F., Luo M. and Turkson R.F., 2016, Spark Ignition Engine Combustion, Performance and Emission Products from Hydrous Ethanol and Its Blends with Gasoline, *Energies*, 9, 984.

Elfasakhany A., 2015, Investigations on the Effects of Ethanol-Methanol-Gasoline Blends in a Spark-Ignition Engine: Performance and Emissions Analysis. *Eng. Sci. Technol. Int. J.*, 18(4), 713-719.

Elfasakhany A., 2018, Exhaust Emissions and Performance of Ternary Isobutanol-Biomethanol-Gasoline and n-butanol-Bioethanol-Gasoline Fuel Blends in Spark-Ignition Engines: Assessment and Comparison, *Energy*, 830-844.

Eyidogan M., Ozsezen, A.N., Canakci, M. and Turkcan, A., 2010, Impact of Alcohol–Gasoline Fuel Blends on the Performance and Combustion Characteristics of an SI Engine. *Fuel*, 89(10), 2713–2720.

Gnansounou E. and Dauriat A., 2005, Ethanol Fuel from Biomass: A Review. *J. Sci. Ind. Res*., 64(11), 809-821.

İnternet-1, 2020, https://pubchem.ncbi.nlm.nih.gov/compound/702.

İnternet-2, 2020, https://pubchem.ncbi.nlm.nih.gov/compound/Isobutanol.

İnternet-3, 2020, https://pubchem.ncbi.nlm.nih.gov/compound/1049.

Koç M., Sekmen Y., Topgül T. and Yücesu H.S., 2009, The Effects of Ethanol–Unleaded Gasoline Blends on Engine Performance and Exhaust Emissions in a Spark-Ignition Engine. *Renew. Energy*, 34(10), 2101–2106.

Kyriakides A., Dimas V., Lymperopoulou E., Karonis D. and Lois E., 2013, Evaluation of Gasoline–Ethanol–Water Ternary Mixtures Used as a Fuel for an Otto Engine. *Fuel*, 108, 208–215.

Lanzanova T., Vielmo H., Sari R., Dornelles H., Tatsch G., Martins M. and Michels L., 2013, *Performance Analysis of a Spark Ignited Engine Running on Different Water-in ethanol Mixtures*, Society of Automotive Engineers Papers, Warrendale, USA.

Lemaire R., Therssen E. and Desgroux P., 2010, Effect of Ethanol Addition in Gasoline and Gasoline–Surrogate on Soot Formation in Turbulent Spray Flames. *Fuel*, 89(12), 3952–3959.

Li L., Wang M., Peng Z., Song Y., Zhang L. and Yuan W., 2015, Exhaust and Evaporative Emissions from Motorcycles Fueled with Ethanol Gasoline Blends. *Sci. Total Environ*, 502, 627–631.

Lin C.Y. and Wang K.H., 2004, Effects of Diesel Engine Speed and Water Content on Emission Characteristics of Three-Phase Emulsions. *J. Environ. Sci. Health Part A*, 39(5):1345-1359.

Liu H., Hu B. and Jin C., 2016, Effects of Different Alcohols Additives on Solubility of Hydrous Ethanol/Diesel Fuel Blends, *Fuel*, 184, 440-448.

Luo M., El-Faroug M. O., Yan F. and Wang Y., 2017, Particulate Matter and Gaseous Emission of Hydrous Ethanol Gasoline Blends Fuel in a Port Injection Gasoline Engine. *Energies*, 10, 1263.

Martins F., Felgueiras C., Smitkova M. and Caetano N., 2019, Analysis of Fossil Fuel Energy Consumption and Environmental Impacts in European Countries, *Energies*, 12, 964.

de Melo T.C., Machado G.B., Belchior C.R.P., Colaço M.J., Barros J.E.M., de Oliveira E.J., et al., 2012, Hydrous Ethanol–Gasoline Blends – Combustion and Emission Investigations on a Flex-Fuel Engine. *Fuel*, 97:796–804.

Muzikova Z., Pospisil M. and Sebor G., 2009, Volatility and Phase Stability of Petrol Blends with Ethanol, *Fuel*, 88(8), 1351-1356.

Nour M., Attia A.M.A. and Nada S., 2019, Pentanol and Octanol Addition to Hydrous Ethanol/Diesel Blend Achieves Better Blending Stability with Improved Engine Performance and Reduced Emissions. *Fuel*, 251, 10-22.

Olberding, J., Beyerlein, D., Steciak, J. and Cherry, M., 2005, Dynamometer Testing of an Ethanol-Water Fueled Transit Van, *SAE Tech.*, 2005-01-3706.

Rajan S. and Saniee F.F., 1983, Water–Ethanol–Gasoline Blends as Spark Ignition Engine Fuels. *Fuel*, 62 (1), 117–121.

Rao, R.N., Silitonga, A.S., Shamsuddin, A.H., Milano J., Riayatsyah M.I., Sebayang A.H., Bin Nur T., Sabri M.,

Yulita M.R. and Sembiring R.W., 2020, Effect of Ethanol and Gasoline Blending on the Performance of a Stationary Small Single Cylinder Engine. *Arab. J. Sci Eng.*, 45, 5793–5802.

SAE, 2004, *Engine Power Test Code – Spark Ignition and Compression Ignition – Net Power Rating*, SAE J 1349.

Schifter I., Diaz L., Gomez J.P. and Gonzalez U., 2013, Combustion Characterization in a Single Cylinder Engine with Mid-Level Hydrated Ethanol–Gasoline Blended Fuels. *Fuel*, 103, 292-298.

Shirazi S.A., Abdollahipoor B., Martinson J., Reardon K.F. and Windom B., 2018, Physiochemical Property Characterization of Hydrous and Anhydrous Ethanol Blended Gasoline, *Ind. Eng. Chem. Res.* 57(32), 11239–11245.

Suarez-Bertoa R., Zardini A.A., Keuken H. and Astorga C., 2015, Impact of Ethanol Containing Gasoline Blends on Emissions from a Flex-Fuel Vehicle Tested over the Worldwide Harmonized Light Duty Test Cycle (WLTC). *Fuel*, 143, 173-182.

Thakur A. K., Kaviti A. K., Mehra R. and Mer K. K. S., 2017, Progress in Performance Analysis of Ethanol Gasoline Blends on SI Engine, *Renew. Sustain. Energy Rev.*, 69, 324-340.

Venugopal, T., Sharma A., Satapathy S., Ramesh A. and Gajendra Babu M., 2013, Experimental Study of Hydrous Ethanol-Gasoline Blend (E10) in a Four-Stroke Port Fuel Injected Spark Ignition Engine, *Int. J. Energy Res*., 37(6): 638-644.

Wang B., Sun L. S., Su S., Xiang J., Hu S. and Fei H., 2012, A Kinetic Study of NO Formation During Oxy-Fuel Combustion of Pyridine. *Appl. Energy*, 92, 361-368.

Wang X., Chen Z., Ni J., Liu S. and Zhou H., 2015, The Effects of Hydrous Ethanol Gasoline on Combustion and Emission Characteristics of a Port Injection Gasoline Engine. *Case Stud. Therm. Eng.*, 6, 147-154.

Wicker R.B., Hutchison, P.A., Acosta, O.A. and Matthews, R.D., 1999, Practical Considerations for an E85-Fueled Vehicle Conversion. *SAE Tech. Pap.*, 1999-01-3517.

Yüksel F. and Yüksel B., 2004, The Use of Ethanol–Gasoline Blend as a Fuel in an SI Engine. *Renew. Energy*, 29(7), 1181–1191.

Zhang, W., Shu, G., Chen, Z., Shen, Y. and Weng, J., 2012, Chemical Kinetics of Ignition Timing of Diesel Engine Fueled with Water Emulsion Diesel. *Nongye Gongcheng Xuebao/Transactions of the Chinese Society of Agricultural Engineering*, 28, 59-66.

Zhuang Y. and Hong G., 2013, Primary Investigation to Leveraging Effect of Using Ethanol Fuel on Reducing Gasoline Fuel Consumption. *Fuel*, 105, 425–431.