Original Research Article

# Comparative exergy analysis of oxygenated fuel additives in a spark-ignition (SI) engine

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**ABSTRACT**

The effects of oxygenated fuel additives have been investigated based on the second law (exergy analysis) of thermodynamic in an SI engine. Exergy terms such as the total cylinder exergy, exergy transfers via heat transfer and work, fuel chemical exergy and irreversibility were computed for closed part of the engine cycle. Additionally, the exergy distributions, the brake power, brake specific fuel consumption (BSFC), first (energy) and second law (exergy) efficiencies were determined. The experimental data, especially the measured cylinder pressure data, were used to calculate the exergy terms with a home-made code. Test results showed that when compared with gasoline operation, the peak cylinder pressure for M10, E10, and S10 was increased by 18.65%, 12.75% and 15.52%, respectively, and also shifted towards to TDC. In addition, the energy and exergy efficiency decreased with the addition of methanol, ethanol, and solketal. The maximum reduction in the exergy efficiency occurred for the S10, and this reduction was determined as about an 8.42%. The results also revealed that the gasoline blends containing 10% methanol, ethanol, and solketal were an unfavorable choice from the second-law perspective, due to the reduction in the exergy.

Keywords: Performance, Additives, Solketal, Gasoline, Exergy Analysis

## 1. Introduction

In recent decades oxygenated fuels have been taken more attention due to their superior combustion and exhaust emissions. Adding oxygenated fuels to base gasoline has been used as an effective way to reduce CO, HC and PM emissions. Moreover, fuel additives have been used to enhance the quality and efficiency of fuels used in the internal combustion engines for a long time. A number of fuel additives are used in literature. An additive that is based on HC and does not produce any extra harmful emissions, and also contains oxygen to improve the combustion is preferred. Currently, alcohols are the most popular additives as octane boosters and as a partially oxidized fuel in gasoline fuel. The influences of methanol, ethanol, or their mixtures with gasoline on the performance parameters, combustion characteristics and exhaust emissions of SI engines were extensively studied in the literature [1-15]. In one of these studies, the effects of added methanol into gasoline on engine performance was investigated in an SI engine by Abu-Zaid et al. [1]. The results of this study indicated that methanol addition increased the octane number of the fuel, and improved the engine performance. Similarly, Bilgin and Sezer [4]

investigated the effect of methanol presence in gasoline on engine performance. The result indicated that brake mean effective pressure (BMEP) was its maximum at the blend of 5% methanol, and of 95% gasoline by volume. In another study, Shenghua et al. [9] conducted an experimental study on an SI engine using gasoline blends containing methanol at varying ratios of 10% to 30% as fuel. They reported that the brake thermal efficiency (BTE) increased whereas the engine torque and power decreased as increase ratio of methanol in the gasoline blends. Koc et al. [8] studied the effects of gasoline blends containing ethanol at high ratios such as 50% and 85% on the engine performance and exhaust emissions at various compression ratios. They reported that increasing the compression ratio and the ethanol concentration in gasoline blends decreased the exhaust emission such as CO, NOx, and HC, and also increased the brake power and BSFC. In another study, an experimental study was performed by Schifter et al. [10] to examine the effects of gasoline blends containing 0% to 20% ethanol on engine performance and exhaust emissions. The results indicated that the combustion process slowed down and the cyclic dispersion increased when the volume concentration of ethanol in gasoline blends reached to 20%. Costa and Sodre [5] tested the hydrous ethanol (6.8% water content) and the E22 blend (containing 22% of ethanol) on a FIAT engine. They reported that the hydrous ethanol caused a higher BSFC and BTE than the ethanol-gasoline blend in the studied speed range.

In recent years, solketal have been used as a gasoline additive [16, 17]. Nevertheless, the usage of solketal as a fuel additive to biodiesel was also investigated [18]. Solketal can be produced from the catalytic reaction of glycerol with acetone [19]. Glycerol is the major by-product of biodiesel production. Acetone is used as a basic ingredient in many industrial processes. The global acetone production is expected to exceed 8.44 million tons at the end of 2017. The intensive use of acetone causes in large quantities of acetone containing wastes. These acetone wastes can be extremely harmful to human health and the environment. One effective way of disposing of such wastes is the catalytic conversion of glycerol with acetone.

By this way, acetone wastes can be converted into carbon dioxide and water. Alptekin and Canakci [17] tested the pure gasoline and the blend containing 9% solketal in order to research the engine performance and exhaust emission characteristics of an SI engine.

The exergy (availability) analysis for internal combustion engines has been used as a powerful tool to determine the origin of irreversibilities and acquiring more precise information about engine efficiency [20-23]. Sezer et al. [21] examined the effects of methanol and ethanol on the exergy equilibrium. They concluded that the usage of methanol and ethanol as engine fuel were appropriate from the second law perspective owing to the lower heat and exhaust losses, and the less entropy production. Similarly, Gallo and Milanez [24] reported that the use of ethanol reduces combustion irreversibility. Caton [25] investigated the destruction of the exergy associated with combustion processes. It was seen that the increase in combustion temperatures reduced the destruction of the exergy because of the efficient combustion process.

In the literature, most research has been focused on examining the effects of methanol and/or ethanol-gasoline mixtures on engine performance and exhaust emissions. However, there are very few studies on the usage of solketal-gasoline blends as fuel in SI engines. Furthermore, the effects of methanol, ethanol and solketal blends were not investigated based on the second law of thermodynamics. For these reasons, the usage of methanol, ethanol, and solketal as fuel additives in an SI engine has been investigated from the thermodynamic first and second law perspective. In addition, the results of all fuels tested were compared with each other.

## 2. Experimental methods

In the experiments, ethanol-gasoline, methanol-gasoline, solketal-gasoline blends and gasoline were used as fuel. Solketal of 97% purity, methanol, and ethanol of 99% purity were purchased from MERCK. Some properties of methanol, ethanol, solketal, and gasoline are shown in Table 1, from References [17, 26, 27]. In the European Union member countries and USA different oxygenated fuels are blended with gasoline to get the ratio of 3.7 %wt. oxygen. The oxygenated fuel content of the

most gasoline sold does not exceed 10% by volume. Therefore, in this study, the methanol, ethanol, and solketal blends with gasoline were blended by a volume basis in a concentration of 10% and 90% gasoline, and the gasoline blends containing 10% methanol, ethanol, and solketal were named as M10, E10, and S10. In engine tests, a water-cooled, single cylinder, four-stroke, SI engine was used. The test setup is shown in Figure 1. The experiments were conducted under wide-open throttle (WOT) conditions for a rated speed of 1500 rpm to evaluate the engine performance and combustion characteristics. The specifications of the test engine and measurement system were shown in Table 2. During the experiments, all measurements were repeated at least three times at each test point and the averaged values were used to minimize the systematic error. The uncertainty of the calculated variables (Equations 1-3) was performed using the Root Sum Square (RSS) method [28]. The uncertainties of the calculated results and the measurement accuracies were given in Table 3.

Table 1. Some Physical and Chemical Properties of Fuels [17, 26, 27]

| Property | Gasoline | Methanol | Ethanol | Solketal |
|---|---|---|---|---|
| Molecular Mass (kg/kmol) | 95-120 | 32.04 | 46.07 | 132.16 |
| Oxygen Content (wt%) | - | 49.93 | 34.72 | 36.36 |
| Density (g/cm$^3$) | 760 | 796 | 790 | 1040 |
| Latent heat of vaporization (kJ/kg) at 20 ºC | 307 | 1147 | 873 | 374 |
| Stoichiometric air/fuel ratio (AFR) | 14.6 | 6.5 | 9.0 | 7.8 |
| Lower heating value (kJ/kg) | 43000 | 20050 | 26950 | 25900 |



1. Computer
2. Control Panel
3. Air Flow Meter
4. Fuel Flow Meter
5. Exhaust Gas Calorimeter
6. Exhaust Gas Analyser
7. Shaft Encoder
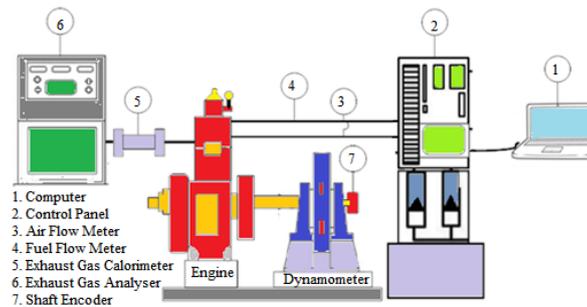
Figure 1. Schematic view of experimental arrangement

Table 2. Specifications of test engine and measurement system

| Type | single cylinder, water cooled, four stroke |
|---|---|
| Dimensions: bore /stroke, mm | 87.5/ 110 |
| Compression ratio | 8, CR variation: 6:1-10:1 |
| Cylinder volume, cm$^3$ | 661 |
| Maximum brake power | 4.5 kW @ 1800 rpm |
| Spark timing | 10 CA bTDC, Spark variation: 0-70 CA bTDC |
| Fuel System | Carbureted |
| Dynamometer | Type: Eddy current, water cooled, with the loading unit |
| Speed, rpm | 1500 rpm, Speed range: 1200-1800 rpm |
| Airflow transmitter | Pressure Transmitter, Range (-) 250 mm WC |
| Fuel flow transmitter | DP transmitter, Range 0-500 mm WC |
| Crank Angle Sensor | Resolution 1 Deg, Speed 5500 rpm with TDC pulse |
| Piezosensor | PCB Piezotronics; Combustion: Range 350Bar |

Table 3. Measured and calculated uncertainties in engine test

| Measurements | Accuracy |
|---|---|
| Brake Torque | ±1.5% |
| Engine Speed | ±0.06% |
| $\dot{m}_{air}$ | ±0.2% |
| $\dot{m}_f$ | ±0.25% |
| $P_{cyl}$ | ±0.2% |
| **Calculated Parameters** | **Uncertainty** |
| Brake Power (kW) | <±1.5% |
| BSFC (gr/kWh$^{-1}$) | <±1.52% |
| $\eta_l$ and $\eta_{ll}$ | <±1.6% |

## 2.1. Engine Performance Characteristics
In this study, brake power (BP) obtained at the crankshaft was calculated by the following expression:

$$BP = \frac{2\pi n T}{60 \times 1000} \qquad (1)$$

where BP is the brake (effective) power (kW); T is the engine torque output (Nm); n is the engine speed(rpm).

Brake thermal efficiency (BTE) was computed by

$$\eta_I = \frac{BP}{\dot{m}_f \, LHV_f} \times 100 \qquad (2)$$

where $\eta_I$ is brake thermal efficiency (first law efficiency) (%); $\dot{m}_f$ is mass fuel rate into the cylinder (kgs$^{-1}$), and $LHV_f$ is the lower heating value of the fuel (kJkg$^{-1}$).

BSFC (gkW$^{-1}$h$^{-1}$) is the fuel flow rate per brake power output and was computed as

$$BSFC = \frac{(3600 \times 1000) \times \dot{m}_f}{BP} \qquad (3)$$

## 2.2. Exergy Analysis
The cylinder pressure vs. crank angle data from 50 consecutive cycles was recorded. The average pressure data of these 50 consecutive cycles were obtained. The homemade software was processed to obtain second law parameters from the averaged pressure data of 50 cycles. Exergy terms were calculated by first law analysis of the averaged cylinder pressure-crank angle data. The detailed analyses according to the second law analysis of engine operation have been given in [23, 29]. The exergy balance equation with considering fuel chemical exergy for the closed part of an engine cylinder, on an $^o$CA basis, can be written as [30].

$$\frac{dE_{cyl}}{d\theta} = \frac{dE_Q}{d\theta} - \frac{dE_W}{d\theta} + \frac{dE_f}{d\theta} - \frac{dI_{comb}}{d\theta} \qquad (4)$$

The exergy transfer associated with heat (E$_Q$), and the exergy associated transfer with work (E$_W$) were computed with the following formulas;

$$\frac{dE_Q}{d\theta} = \left(1 - \frac{T_o}{T_{cyl}}\right)\frac{dQ}{d\theta} \qquad (5)$$

$$\frac{dE_W}{d\theta} = \left(p_{cyl} - p_o\right)\frac{dV}{d\theta} \qquad (6)$$

where the subscript "o" refers to the dead state condition. The temperature and pressure of the reference environment (dead state conditions) were taken as 298.15 K and 101.325 kPa in this study [31].

The fuel exergy (E$_f$) was computed with

$$\frac{dE_f}{d\theta} = \frac{mf}{m}\frac{dx_b}{d\theta}e_f \qquad (7)$$

where $e_f$ (kJkg$^{-1}$) is the specific fuel exergy, which was computed by following formula;

$$e_f = \frac{(\Delta G)_{T_o,p_o}}{(\Delta H)_{T_o,p_o}} \times (LHV_f) \qquad (8)$$

Exergy of a system is not a conserved property like energy. Because, exergy is destroyed by processes named as irreversibility such as friction, mixing processes, combustion, and heat transfer across a finite temperature gradient. The exergy destroyed or irreversibility was calculated from the change in entropy owing to the combustion as follows;

$$\frac{dI}{d\theta} = T_o \frac{d\sigma}{d\theta} \qquad (9)$$

$$\frac{d\sigma}{d\theta} = \frac{d(m \times s)}{d\theta} \qquad (10)$$

where σ is the rate at which entropy occurs due to combustion irreversibility.

Exergy balance of engine for closed part of the engine was obtained as follows;

$$\frac{dE_{cyl}}{d\theta} = \left(1 - \frac{T_o}{T_{cyl}}\right)\frac{dQ}{d\theta} - \left(p - p_o\right)\frac{dV}{d\theta} + \frac{mf}{m}\frac{dx_b}{d\theta}a_f - \frac{dI_{comb}}{d\theta} \qquad (11)$$

## 3. Results and discussions
Figure 2 shows the changes in engine performance parameters such as brake power and BSFC of the tested fuels. This figure indicated that the use of M10, E10, and S10 increased the brake power by a 7.76%, 11.04%, and 9.85% respectively, as compared to gasoline. These increases in brake power could be expressed by the higher enthalpy of vaporization and oxygen content of methanol, ethanol, and solketal. As seen in Table 1, compared with gasoline, methanol, ethanol, and solketal contain oxygen, and this enhances the combustion process and that leads to reduce the HC and CO emissions and increase the $CO_2$ emissions. In addition, the methanol, ethanol, and solketal have a higher heat of evaporation than gasoline, this decreases the combustion temperature. This decrease in combustion temperature reduces brake power and torque; but the higher volumetric efficiency causes to improve fuel combustion and, in turn, increases the brake power and the torque.

Figure 2 also shows the BSFC for test fuels. BSFC for G, E10, M10, E10, and S10 was calculated by 389.40, 416.23, 427.99 and 424.85

g/kWh, respectively. For G, M10, E10, and S10, the in-cylinder pressure and the mass fraction burned, with respect to crank angle is depicted in Figure. 3. The cylinder pressure was getting maximum value for M10, while it was a minimum value for gasoline operation. The increment in peak cylinder pressure was observed by 18.65%, 12.75%, and 15.52% for M10, E10, and S10, respectively, when compared with gasoline engine operation.
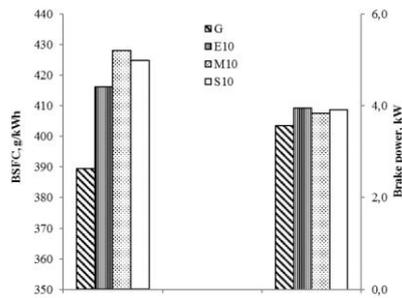


Figure 2. The variation in the engine performance parameters for the tested fuels
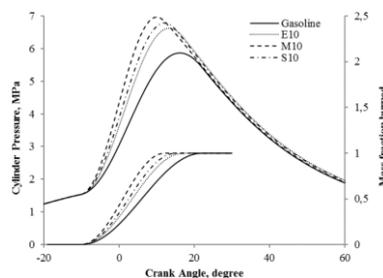


Figure 3. The variations in the cylinder pressure and the mass fraction burned for the tested fuels, as a function of crank angle

This is due to the laminar flame speed of the methanol, ethanol, and solketal have higher than gasoline. With the addition of these additives to gasoline, the burning rate of fuel increases, and the combustion duration decreases. It was determined that the total combustion duration (overall burning angle) were 26 CA, 22 CA, 20 CA and 18 CA for gasoline, E10, S10, and M10, respectively. These results are agreement with results in the literature [32]. Figure 4 indicates the changes in exergy terms as a function of crank angle for the tested fuels. As shown in this Figure, the variations of exergy terms for test fuels are similar but different in magnitude. Before the combustion started, so that the chemical exergy of the fuel was constant. After combustion started, the fuel chemical exergy started to decrease due to heat conversion, and it was zero at the end of combustion. The total exergy in engine cylinder increased with the effect of compression work despite the heat transfer, and then it decreased with the effects of

heat and work transfer and combustion irreversibility. The irreversibility dramatically increased during the combustion stroke, and it reached its maximum value at the end of combustion. The exergy transfers by work, as well as exergy transfer with heat transfer sharply increased during combustion and expansion strokes. Figure 5 shows the variation in exergy transfers via heat transfer and work, fuel exergy, and combustion irreversibility for the tested fuels.

Figure 5a-5b shows the effects of different blends and gasoline on the exergy transfer with work and heat transfer for the closed engine cycle. As illustrated in this figure, the maximum exergy transfers associated with heat and work occurred for M10 while they fall to lower values for S10, and E10, and to a minimum value for gasoline. This is because, the M10, S10, E10 exhibited the higher combustion temperature and cylinder pressure as compared to gasoline. Figure 5c clearly shows that each tested fuels have different fuel chemical exergy values. The fuel chemical exergy increased by adding of methanol, ethanol, and solketal due to increase in the amount of fuel consumption.

In addition, a difference occurred in the slopes of the chemical exergy lines for blends due to the reduction in combustion duration. As shown in Figure 5d, while the highest irreversibility was achieved for gasoline, and then for M10 and S10 fuels, and the lowest for E10. It is well known that entropy generation occurs due to irreversibilities nature of the combustion. The addition of methanol, ethanol, and solketal improved the combustion due to their oxygen content results in a decrease in irreversibility. Because the increase of combustion temperatures decreases the exergy destruction in the combustion process [25].

Figure 6 shows the exergy distributions of the fuel chemical exergy for the tested fuels. The percentage of fuel chemical exergy exchanged through work were calculated as 36.34, 35.87, 35.82 and 39.11% for M10, E10, S10, and gasoline, respectively. Similarly, the percentage of fuel chemical exergy exchanged through heat were also calculated as 14.99, 14.69, 14.73 and 16.06% for M10, E10, S10, and gasoline, respectively. The percentage of fuel chemical exergy exchanged through work and heat for the blends have lower than gasoline.
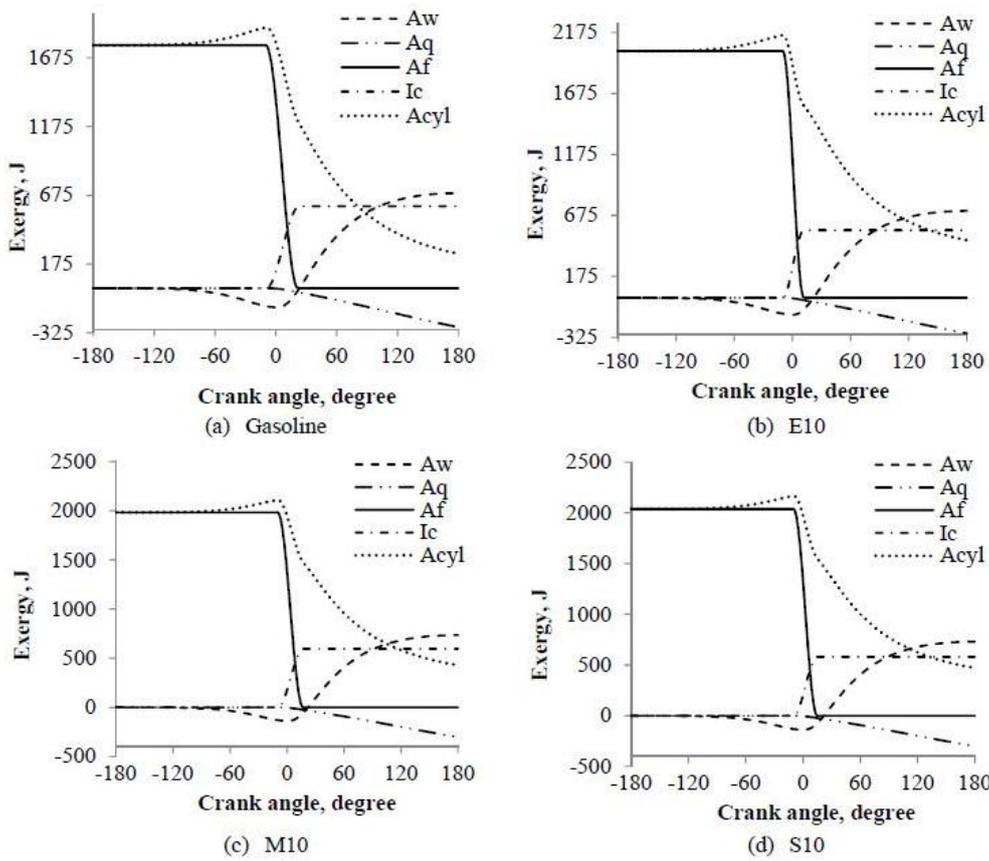
Figure 4. The variation in (a) exergy for gasoline, (b) exergy for ethanol-gasoline blend, (c) exergy for methanol-gasoline blends, and (d) exergy for solketal-gasoline blend
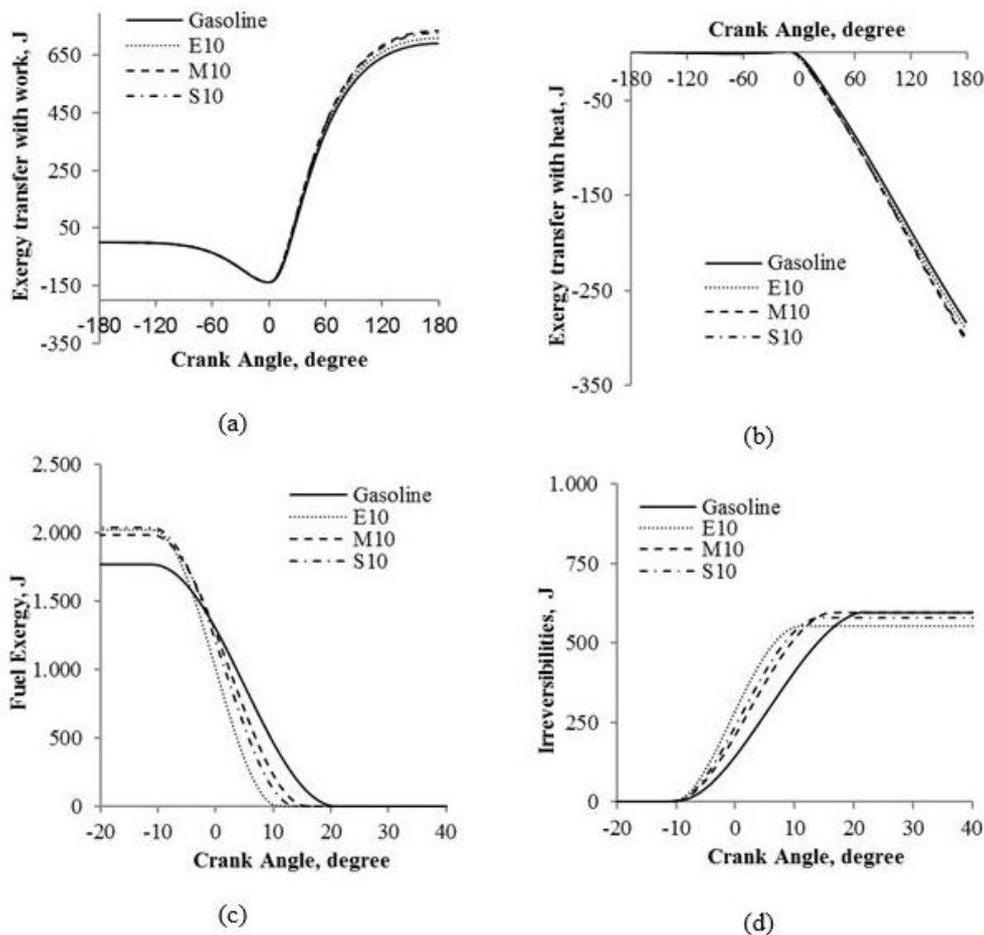


Figure 5. The variation in (a) exergy transfer with work, (b) exergy transfer with heat, (c) fuel exergy, and (d) irreversibility for the tested fuels

Although the combustion temperatures of the blends were higher than that of the gasoline, the percentage of exergy transfer with heat for the blends decreased. This is because of the limited increase in the magnitude of the heat transfer due to the shorter combustion duration relative to the increase in fuel exergy. In addition, while the magnitude of the exergy transfers with work increases by the addition of additives, however the percentage of fuel chemical exergy exchanged through work decreases, because the increase in the fuel exergy would not be converted to work in the same rate [30]. In addition, the percentage of fuel chemical exergy exchanged through irreversibility (exergy destruction) was calculated as 29.44, 27.92, 28.48 and 33.76% for M10, E10, S10, and gasoline, respectively. The percentage of fuel chemical exergy exchanged through irreversibility for blends have lower than gasoline, because of the higher combustion temperature, and lower combustion duration. The percentage of fuel chemical exergy exchanged through exhaust gases were about 19.23, 21.51, 20.97 and 11.07% for M10, E10,

S10, and gasoline, respectively. The exhaust exergy distributions of the blends have higher than gasoline. This means only a portion of fuel exergy was converted into useful work. Figure 7 shows the change in first and second law efficiencies of the tested fuels. As shown in the figure, the first law efficiency was calculated as 20.66, 20.89, 20.52 and 21.5% for M10, E10, S10, and gasoline, respectively. As seen, the first law efficiency slightly decreased for M10, E10, and S10, when compared to gasoline. In addition, the second law efficiency was calculated as 35.87, 36.34, 35.87 and 39.11% for M10, E10, S10, and gasoline, respectively. Similarly, the second law efficiency slightly decreased with the addition of methanol, ethanol, and solketal, while the maximum reduction occurred for S10. This reduction in second law efficiency for S10 was calculated as a rate of 8.42%. According to these results, the gasoline blends containing 10% methanol, ethanol, and solketal were an unfavorable choice from the second-law perspective due to the reduction in second law efficiencies.
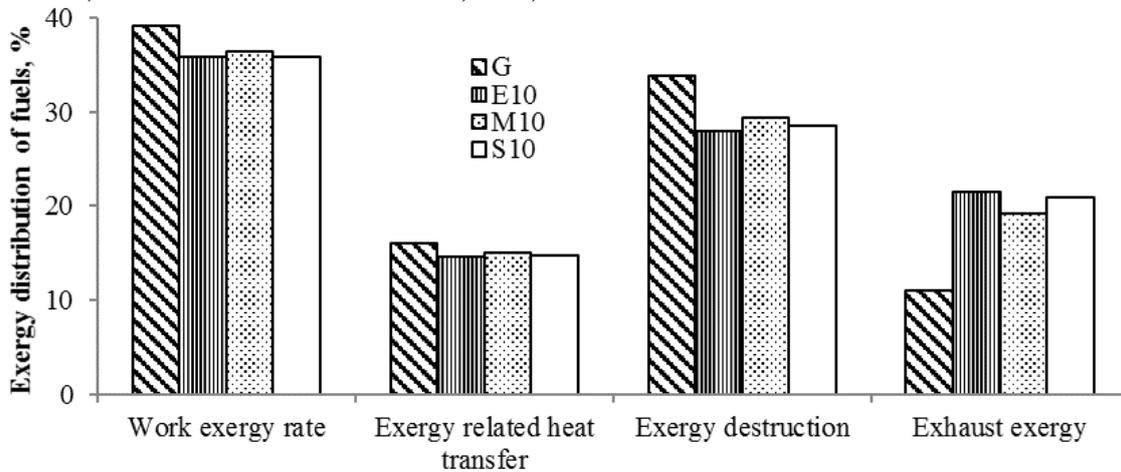


Figure 6. Exergy distribution of the tested fuels
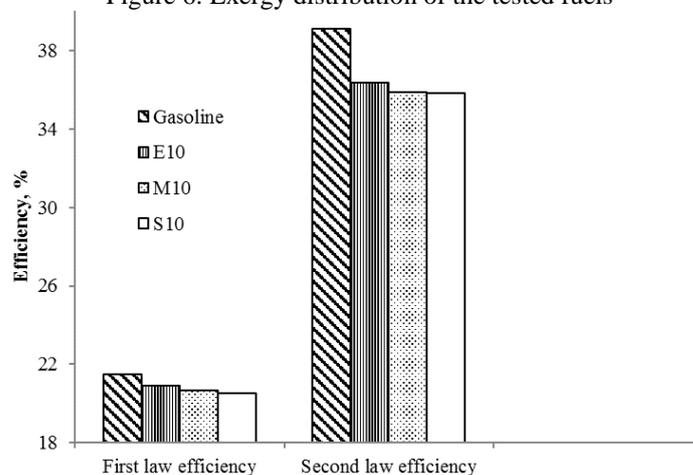


Figure 7. The variation of first and second law efficiency for the tested fuels

## 4. Conclusions

In this present study, a comparative exergy analysis has been done to investigate the usage of gasoline additives containing oxygen in SI engines. The following conclusions can be derived from the obtained results.

1. The brake power and BSFC have significantly increased fueled as M10, E10, and S10 when compared to gasoline.
2. When compared with gasoline operation, the maximum cylinder pressure has increased, and the peak cylinder pressure also shifted towards to TDC, for M10, E10, and S10.
3. The exergy transfers associated with heat and work have realized as a maximum for M10, lower values for the S10 and E10, and minimum value for gasoline.
4. The values of the fuel chemical exergy, and the slopes of the chemical exergy lines have increased for the blends.
5. The values of irreversibility have been maximum for gasoline, lower for M10 and S10, and also minimum for E10.
6. Exergy distributions of the total input fuel exergy for M10, E10, and S10 have shown to be a reduction in combustion irreversibility and exergy transfer with heat, while the exhaust exergy and the exergy transfer with work increased.
7. The first law efficiencies have slightly decreased for M10, E10, and S10 when compared to gasoline case. The reduction in the second law efficiencies has been more obvious.
8. The gasoline blends containing 10% methanol, ethanol, and solketal are an unfavorable choice from the second-law perspective, due to the reduction in second law efficiencies. On the other hand, the methanol, ethanol and solketal addition have caused a progressive decrease in the combustion irreversibility. This is favorable from the second-law perspective.

The adding methanol, ethanol, and solketal of 10% by volume to gasoline have a negative effect on thermal and exergetic efficiencies. In this study, constant spark timing was used in all experiments. Exergetic efficiency of these blends could be increased by adjusting the ignition timing. Therefore, it should be done further studies to optimize the engine operating conditions for the blends from the first and second law perspective.

## Nomenclature

| | |
|---|---|
| BP | power (kW) |
| e | specific availability on mass base (J/kg) |
| E | exergy (availability) (J) |
| G | gibbs free energy (J) |
| H | enthalpy (J) |
| I | irreversibility (J) |
| LHV | lower calorific value (kJ/kg) |
| m | mass (kg) |
| n | rotational speed of the crankshaft (rpm) |
| p | pressure (Pa) |
| Q | heat (J) |
| s | mass specific entropy (J/kg K) |
| T | temperature (K) |

*Greek letters*

| | |
|---|---|
| $\eta_I$ | thermal (first law) efficiency |
| $\eta_{II}$ | exergetic (second) law efficiency |
| $\theta$ | crank angle (deg) |
| $\sigma$ | entropy generation |

*Subscripts*

| | |
|---|---|
| b | burned |
| br | brake |
| comb | combustion |
| cyl | cylinder |
| f | fuel |
| o | dead state condition |
| q | associated with heat transfer |
| W | associated with work transfer |

*Abbreviation*

| | |
|---|---|
| BMEP | brake mean effective pressure |
| BSFC | brake specific fuel consumption |
| CA | crank angle |
| WOT | wide open throttle |

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