

Review article

A review on higher alcohol of fusel oil as a renewable fuel for internal combustion engines: Applications, challenges, and global potential



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ARTICLE INFO

Keywords:

Higher alcohols
Fusel oil
Combustion
Emission
Internal combustion engine

ABSTRACT

Global warming, climate change, crisis about the energy price, and supply are the main issues in the world and the petroleum-based energy supplement is the main responsible for these problems. More specially, environmental concerns peaked after the critical carbon dioxide level exceeded. Increasing the percentage of clean and renewable energy sources while compensating energy demand became mandatory than ever before. At that point, alcohols are attractive alternative fuels to gasoline and diesel, especially in terms of harmful exhaust emissions. The effects of the typical alcohols such as ethanol methanol, butanol etc., were examined in detail up to date. Fusel oil is a higher alcohol obtained during the fermentation process as a byproduct, and its usage in internal combustion engines took attention during the last decade. In this study, a comprehensive review was conducted about the potential usage of the fusel oil in internal combustion engines as a renewable and clean energy source. The potential production of the fusel oil and its properties as a fuel were discussed. The engine performance, combustion, and emission characteristics of the fusel oil on spark ignition, compression ignition, and homogeneous charge compression ignition engines were also examined in detail. The findings indicated that the performance characteristics of fusel oil are similar to ethanol, which may increase the application area of it.

1. Introduction

Fossil-based petroleum fuels are the main energy sources for a wide range of sectors, especially transportation [1–4]. The chemical energy of the fossil fuels is released after the oxidation process which requires a certain air/fuel ratio. If the stoichiometric combustion conditions can be provided, exhaust products are acceptable except carbon dioxide (CO_2). It is well known that theoretical stoichiometric combustion is not possible for an internal combustion engine even for an atmospheric burner [5–8]. For an internal combustion engine, it is very hard to provide proper mixture, enough time, and homogeneous temperature distribution in the cylinder. The maximum combustion efficiency is generally less than 96–97% for both spark ignition and compression ignition engines. Therefore, incomplete combustion products carbon monoxide (CO) and unburned hydrocarbon (UHC) emissions are inevitable. Considering also nitrogen oxide (NOx) and CO₂ emissions, the extent of the damage caused by exhaust gases to the environment is

obvious [9–14]. Among these harmful gases, as a greenhouse gas, CO₂ is the main responsible for climate change, and atmospheric CO₂ level has passed over the critical 400 ppm limit in 2016. This has led to increased environmental concerns [12,15–17].

Searching renewable and environmentally friendly fuel is going on for decades because of both the harmful aspects of fossil fuels and depletion risks of it [14,18–22]. Besides, the studies on advanced vehicle technologies such as hybrid electric vehicles, fully electric vehicles, fuel cell, solar technologies etc. accelerated in the past 30 years [23–29]. However, most of those are still under the developing process, and it does not seem to be possible to find a wide usage area in the short and medium-term because of several issues. For this reason, the power demand of the vehicles will be provided by internal combustion engines for a long time. That makes mandatory to use cleaner fuels in internal combustion engine. Oxygenated fuels are the most popular alternative fuels because of their oxygen content that improves combustion in the cylinder, and it allows to reduce emissions on the source [30–33].

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Nomenclature

RSM	response surface method
CO ₂	carbon dioxide
UHC	unburned hydrocarbons
BSFC	brake Specific fuel consumption
IMEP	indicated mean effective pressure
RON	research octane number
RON40	40% isoctane and 60% n-heptane
CV	calorific value
F10	90% gasoline + 10% fusel oil
FAWE10	90% pure gasoline + 10% fusel oil after water removal

FBWE10	90% pure gasoline + 10% fusel oil after water removal
BTE	brake thermal efficiency
NO _x	nitrogen oxides
CO	carbon monoxide
MTBE	methyl <i>tert</i> -butyl ether
HCCI	Homogeneous charge compression ignition
CR	compression ratio
ITE	indicated thermal efficiency
E25	25% ethanol and 75% n-heptane
FAWE20	80% pure gasoline + 20% fusel oil before water removal
FBWE20	80% pure gasoline + 20% fusel oil before water removal
F0	Gasoline

Another attractive side of oxygenated fuels is that most of them are produced from renewable bio-based sources such as sugarcane, several seed oils, waste oils, beets etc. [34–40]. Alcohol fuels, which can be utilized as an oxygenated fuel in internal combustion engines, are currently used energy sources for transportation, especially for passenger cars. There is no doubt that ethanol has the largest percentage in terms of usage in passenger vehicles among the other alcohol types. Its non-toxic structure and the abundant producibility capacity from bio-sources are the main reasons for wide application of it. Its high hydrogen/carbon ratio, high research octane number, high flame propagation speed, low volatility emissions, safe storage, and transportation features also make it a reliable fuel, especially for spark-ignition engines [41–47].

Fusel oil takes attention by researchers due to its ethanol like features. Fusel oil, which has an oxygenated chemical structure, is a by-product of the fermentation process, and its research octane number is over 105 as like as ethanol [48–50]. Therefore, it seems to be an appropriate alternative fuel, particularly for spark-ignition engines. Fusel oil is placed as an oily layer after removing the alcohol from the fermented mixtures including some amount of water. This secondary layer was firstly named as fousel. The meaning of the fousel in German is the evil spirit. This name might have been given to fusel oil because of its bad odor and dark brown color. In 1984, Dumas conducted a study to determine the boiling point of fusel oil obtained from fermented potato. He determined that the boiling point of the fusel oil is between 130 and 132 °C [51]. Up to date, fusel oil was mostly used to produce isoamyl acetate, biodiesel, bio-lubricants [52–56]. There are a few applications using it as an energy source in distilleries as well [44]. There is no study about the usage of the fusel oil in internal combustion engines until 2012 [57].

The production of the fusel oil is possible by distillation of any fermented mixture. Its structure varies due to the type of fermented product. A typical fusel oil contains higher alcohols such as i-amyl alcohol, i-butanol, i-propanol. It also contains some amount of ethanol and miscellaneous alcohols as well as moisture content [58]. The fusel oil is a higher alcohol by considering its chemical structure. Higher alcohols, which have a carbon number from 3 to 20, also have the potential to be evaluated as fuel in internal combustion engines. Atmanlı [59] conducted a study examining the effects of higher alcohols such as propanol, n-butanol, and pentanol by blending diesel–biodiesel. It was reported that the higher alcohols improved the cold filter plugging point of the diesel–biodiesel blends. However, higher alcohols slightly reduced kinematic viscosity, lower heating value, density, and cetane number. NO_x emissions decreased while carbon monoxide emissions increased with the use of all three higher alcohols. Şen [60] investigated the effect of injection pressure on a diesel engine powered with propanol-diesel fuel blends. Combustion duration shortened by using propanol. Another butanol-diesel study was conducted by Sarıköç et al [61]. It was found that the butanol percentage affected energy-exergy values. The ternary blend of diesel-biodiesel-butanol was found to be similar to petro-diesel in terms of energy-exergy efficiency.

Moreover, emission levels of the ternary fuel blend was lower than eurodiesel. Santhosh et al. [62] experimentally investigated the performance and emission characteristics of a common rail direct injection diesel engine using 1-pentanol and diesel fuel blends. Exhaust gas recirculation was also utilized in the study. It was found that 1-pentanol negatively affected brake thermal efficiency and brake specific fuel consumption while it reduced the NO_x emissions. It was also reported that the ignition delay increased by using 1-pentanol and diesel fuel blends because of the lower cetane rating of the 1-pentanol. Uslu and Çelik [63] tested the isoamyl alcohol-gasoline fuel blends in a spark-ignition engine. The combustion and emission characteristics of the engine were investigated in use of isoamyl alcohol. It was reported that isoamyl alcohol positively affected torque and brake thermal efficiency and exhaust emissions. The improvement in engine performance was explained with the oxygenated structure and the higher latent heat of isoamyl alcohol that enhance volumetric efficiency.

As can be seen in the literature review, higher alcohols can be used both in spark-ignition engines and compression ignition engines. Like the other higher alcohols, fusel oil has the potential to be used in both types of those engines. Up to date, several studies were performed by using fusel oil in internal combustion engines. Fusel oil can be considered as a new opportunity for internal combustion engines among the other higher alcohols because all of the studies about the usage of the fusel oil in internal combustion engines were conducted in the last decade. In this study, a comprehensive review was performed about fusel oil potential as a new renewable energy source for internal combustion engines. The next sections of this paper explain the properties of fusel oil as a fuel, the potential production of the fusel oil over the world, the results about the usage of fusel oil in both spark ignition, compression ignition and homogeneous charge compression ignition engines in terms of engine performance, combustion and emissions.

2. Physical and chemical properties of fusel oil relevant to engines

The advantages of using fusel oil (C₅H₁₂O) as a diesel additive have discussed extensively. Fusel oil properties are dependent on different parameters, including the process of decanting/distillation, the condition during the fermentation process, and, more especially, bio-based material used. The composition of fusel oil and its characteristics are depicted in Table 1.

Table 1
Physical characteristics of fusel oil composition [57,64].

Component	formula	(%v/v)	Density (g.cm ³)	Boiling point (°C)
Ethanol	C ₂ H ₆ O	9.58	1	100
Water	H ₂ O	10.3	0.789	78.4
n-propyl alkyl	C ₃ H ₈ O	0.73	0.803	97.1
n-butyl alcohol	C ₄ H ₁₀ O	0.73	0.809	117.73
i-butyl alcohol	C ₄ H ₁₀ O	16.6	0.802	108
i-amyl alcohol	C ₅ H ₁₂ O	63.93	0.810	131.1

Chemical and physical properties of fusel oil are the main parameters in determining the quality of the blended fuel. Such properties could directly affect the combustion process and exhaust emission characteristics of internal combustion engines. The main chemical/physical properties of conventional fossil fuels (i.e., diesel and gasoline), ethanol, and fusel oil are presented in Table 2. [45,65–69]. The high oxygen contained in the fusel oil compared to that of gasoline and diesel is beneficial for combustion quality. The presence of oxygen molecules has beneficial consequences for its characteristics as a fuel additive. The oxygen content also leads to a low air/fuel ratio requirement in comparison with diesel and gasoline fuel. A significant disadvantage of the high oxygen content is that it obviously reduces the heating value [70]. Besides, fusel oil has a higher auto-ignition temperature and flashing point compared to both diesel and gasoline fuel, thus using this fusel at high temperatures is safer.

The main drawback of fusel oil/diesel mixture is the miscibility of fusel oil in neat diesel, especially at low temperatures, which in turn leads to incomplete combustion [71]. This problem can be addressed by adding biodiesel in fusel oil/diesel blends [72]. According to Table 2, it was clearly evident that fusel oil had a higher cetane number compared to ethanol. Generally, the high value of the cetane number of fuels tends to enhance engine brake power and reduce NO_x formation [73]. According to Table 2, fusel oil has advantages over ethanol due to its higher cetane number. The low cetane number could lead to longer ignition delay, engine misfiring, and higher average combustion temperature [74]. Also, fusel oil could be considered to have a positive effect on in-cylinder pressure and injection timing because of its higher viscosity in comparison with diesel and ethanol fuels [75]. Fusel oil would also be considered as a high-density fuel than ethanol. The higher density of fuel causes an increase in mass flow rate and a decrease in fuel leakage during injection, which consequently results in improving the efficiency of the fuel [67]. In addition, the presence of water in fusel oil ranging from 3.5% to 20%, would lead to a lower combustion temperature and heat release rate, which could consequently cause a remarkable NO_x reduction [76,77].

3. Fusel oil production potential in the world

In recent years, alcohol-based fuels, including ethanol [78], butanol [79], and methanol [80], are conventional renewable fuels. Currently, ethanol is one of the most established alternatives to fossil oriented fuels in the US, Brazil, and even South Africa because of its renewability, higher energy density, and also less toxicity compared to methanol fuel [68]. Nowadays, bioethanol makes the main contribution to green transport, corresponding to ~3% of the world's energy consumption for the transport sector. Global ethanol production increased by 1.85% in 2019 compared to 2018 [81]. The United States and Brazil account for the world's largest producers of ethanol, accounting for ~85% of the global production. However, the fermentation process employed is totally different in each of these two countries [82]. The characteristics of bioethanol production in Brazil and the United States have been depicted in Table 3.

Currently, a number of countries have announced an ethanol-gasoline blend to expand the mandatory use of oxygenates fuel additive by 2020. For instance, the government of China announced a program to promote biomass-based ethanol as a renewable fuel blended with gasoline at a ratio of 10% [83]. As shown in Table 4, bioethanol is produced by fermentation of different feedstock in various countries.

The increasing rate in ethanol production has resulted in a considerable increase in fusel oil quantity as a byproduct and the consequent environmental impacts. It is estimated that one ton of raw sugar derived from sugarcane/sugarbeet molasses would yield ~523.8 L of ethanol [84]. Also, one ton of ethyl alcohol would produce ~6.4 L of fusel oil through the distillation process [67]. According to the above-mentioned conversion factor, the total potential for fusel oil production in the world is estimated to be ~550 million liters, which

would be equivalent to ~347 million liter of gasoline and ~325 million liter of diesel fuel. Global fusel oil production by country from 2009 to 2019 is given in Table 5. According to calculations, fusel oil production is very concentrated geographically. The United States produces more than half of the world's fusel oil (54.36%), followed by Brazil (29.63%).

Fusel oil production in European Union was stable in 2019 at ~27 million litres. Fusel oil generation rose ~43% from 2009 to 2019. China ranks fourth for fusel oil production globally during 2009–2019 and produced around 17 million litres.

Methyl *tert*-butyl ether (MTBE) has been used as a fuel additive for decades. The increase in fossil fuel consumption has led to a significant increase in the release of MTBE. MTBE, as a toxic organic compound, represents a serious long-term environmental impact [91]. To address this issue, the fusel oil usage as a oxygenate additive is expected to increase as a result of the phase-out of MTBE in some countries. The usage of fusel oil in internal combustion engines is a promising alternative to diversify and substitute fossil fuel partially without any engine modification in existing CI and SI engines [72]. Nations with ethanol blend mandates are primary fusel oil consumption in the world (Fig. 1) [92]. Therefore, fusel oil can remarkably reduce the reliance on MTBE in those countries.

4. Methods of using fusel oil as an engine fuel

4.1. Using fusel oil in spark ignition engines

Fusel oil, as a long-chain alcohol, has attracted considerable interest due to the positive effect on the engine performance and exhaust emissions. Fusel oil can be used in spark-ignition (SI) engines without any significant engine modification. Several investigations concerning the application of fusel oil in SI engines have been performed, especially in the past ten years (Table 6).

4.1.1. Engine performance

The potential for increased engine brake power/torque fueled with fusel oil has been experimentally validated. İçingür and Calam [49] was the first to report the effect of fusel oil on the engine performance. The improvement in the brake torque was obtained as ~3% at all the tested engine speed i.e. 2000–5000 rpm. The maximum engine torque was reported for a fusel oil blend of 30%. Their results were later confirmed by Calam et al. [64], who reported higher engine brake torque compared to gasoline fuel when combusting F10. A maximum engine brake torque (33.53 Nm) was obtained at the ignition timing of 24° when F10 was used. Different engine loads (25%, 50%, 75%, and 100%) at an engine speed of 2500 rpm were considered as engine working conditions. Studying the impacts of different engine loads/speeds when using fusel oil/diesel blends, Calam et al. [48] reported engine torque had increased by ~5%, when F10 was used. More specifically, they indicated that at a high level of fusel oil ratio, the brake torque increased compared to the brake torque of the engine running with F0. They

Table 2
Physicochemical properties of oxygenated additives compared to diesel/gasoline fuel.

properties	Diesel	Gasoline	Ethanol	Fusel oil
Oxygen content (wt%)	–	–	34.8	18
Density (kg/m ³) at 20 °C	820	765	795	800.3
Lower heating value (MJ/kg)	42.7	43.4	26.8	35.32
Octane number	30	99	100	98.7
Cetane number	55	10	8	42
Latent heat at 298 K (kJ/kg)	270	500	904	874
Flash point (°C)	65	38	13	42
Stoichiometric AFR	14.3	14.7	9	–
Solubility in water (g/L) at 25 °C	Immiscible	Immiscible	Miscible	Miscible
Viscosity, (mm ² /s) at 40 °C	2.929	0.76	1.2	4.162
Auto ignition temperature, °C	~210	~300	434	416

Table 3

The fermentation process in the United States and Brazil [82].

Ethanol characteristics	Brazil	USA
fermentation process	Recycling of the yeast	Without yeast recycling
yield of fermentation	92%	90%
time of process	12 h	60 h
yeast concentration	12%	4%
bioethanol concentration	12% (v/v)	18% (v/v)
suspension of solid particles	<1%	< 30%

attributed the improvement achieved to higher volumetric efficiency and also higher in-cylinder pressure caused by the addition of fusel oil into gasoline fuel. Later in 2015, contrary to the above-mentioned findings, Solmaz et al. [58] stated that the addition of fusel oil into gasoline led to an adverse effect on the engine torque. He reported that the combustion of the fusel oil blend of 50% and 100% led to ~2% and ~6% decrease in engine torque. The lower LHV and water content of fusel oil was highlighted as the main reasons for the decrease in engine torque. In addition, brake thermal efficiency (BTE) variations had a similar trend and decreased ~6% with increasing fusel oil concentration. The best BTE was obtained when the fusel oil ratio of 50% was blended. More specifically, the in-cylinder pressures and heat release rates of F100 and F50 fuels were reportedly decreased, while engine load was increased. He also pinpointed the decrease in IMEP and in-cylinder pressure as a result of the water content of fusel oil, i.e., 10–15%. As mentioned above, the impacts of water content of fusel oil on the combustion characteristic and engine performance have been frequently reported to be negative. In order to improve the quality of fusel oil, in a different study, Awad et al. [93] investigated the effect of moisture content removal from fusel oil on the calorific value (CV) of the blended fuels. They reported that when the water content of fusel oil has decreased from 13.5% to 6.5%, some improvements in CV, brake power, and BTE could be observed. Both IMEP and the rate of in-cylinder pressure rise increased after the reduction of water content to 10%. Meanwhile, for fusel oil/gasoline blends, combustion duration was observed shorter than that of gasoline. They also found that the decrease of the water percentage in the fuel blends has led to a slight improvement in engine power up to ~0.7% compared to the fuel blends before water removal [93]. Later in an experimental work on fusel oil/gasoline mixture, Awad et al. [94] also confirmed the previous observations. They employed multi-objective optimization based on the response surface method (RSM) to estimate the optimal value of engine performance parameters and exhaust emission characteristics fueled with different fusel oil/gasoline blends. The optimal values of engine working conditions were found to be an engine speed of 4499 rpm, fusel oil concentration of 20%, and 55.4% of throttle position. They highlight that water removal from fusel oil blends had a positive effect on BTE, brake torque, and brake power. In a different study, Awad et al. [95] blended different water content of fusel oil in gasoline fuel. The tests were performed at constant engine load 45%, and different engine speeds. Similar findings i.e. an improvement in the combustion and engine performance characteristics, were achieved. They indicated that

the FAWE10 had a better combustion as a result of lower CA50. In an interesting study, the effects of extraction of water on the fusel oil/gasoline mixture characteristics was investigated by Awad et al. [96]. They claimed that the studied emulsion led to an improved BTE and brake power. Also, the reduction of the water content enhanced the combustion temperature and performance because of complete combustion of fuel blend compared to pure gasoline [96]. Simsek and Ozdalyan [97] in the year 2018 investigated the effect of five fusel oil/gasoline blends at various engine loads and fixed engine speed on the engine performance and exhaust emissions. They found that F30 appeared to have higher BTE (~3.98%) and brake torque (3.95%) values compared to neat gasoline. However, a decrease in BTE and engine torque was observed at high levels of fusel oil and pure diesel blends (i.e. 40% and 50%). Very recently, Safieddin et al. [98] focused on the effect of addition of different fusel oil/gasoline mixture (25%, 50%, 75% and 100%) at different engine load levels (20%, 40%, 60%, 80%, and 100%) in a single-cylinder four-stroke engine. RSM was used to optimize engine performance and exhaust emissions. Their finding showed that the addition of fusel oil into pure gasoline led to decrease in BTE and brake torque by 14% and 4%, respectively, due to lower combustion temperature in the cylinder, as shown in Fig. 2.

4.1.2. Fuel consumption

Variations in fuel consumption as a result of fusel oil mixing into pure gasoline has been studied by several investigations. In almost all the previous works, the effect of adding fusel oil to gasoline has been reported to be negative for BSFC, mainly due to a decrease in the CV of the fuel blends. For example, Icingur and Calam [49] observed that the specific fuel consumption (SFC) increased with increasing fusel oil percentage in the fuel mixtures for all engine speeds. Specific fuel consumption increased by up to 7.7% using fusel oil blend of 30% compared to mineral gasoline [57]. The same trend was also observed by Calam et al. [64]. Solmaz [58] extended the latter work by testing F0, F50, and F100 separately. He reported that BSFC for all fuel blends was considerably higher than that of gasoline because of the combined effect of high density and lower heating value (LHV) of fusel oil. Simsek and Ozdalyan [97] and Awad et al. [96] both indicated that 10% fusel oil blended into gasoline fuel led to increased BSFC. Additionally, Simsek and Ozdalyan [97] reported a significant enhancement in SFC as the amount of fusel in the fusel oil-diesel emulsion increased. The increased BSFC of 1.72%, 10.53%, and 30.44% were reported when using F10, F30, and F50, respectively. Similar to the other studies, the gain in BSFC was attributed to the lower heating value of fusel oil. In contrast to the above experimental works, Safieddin Ardebili et al. [98] reported that by increasing the amount of fusel oil included into gasoline up to 20%, BSFC decreased by ~6%. However, they measured a 54% increase in BSFC when fusel oil content increased from 50% to 100%. Generally, it could be concluded that the addition of fusel oil into gasoline would result in an increase in BSFC at various engine loads/speeds.

4.1.3. Exhaust emissions

4.1.3.1. NO_x emissions. While the oxygen content of fusel oil could have a positive effect on the exhaust emission, the water content of this

Table 4

Bioethanol production by different countries and their renewable target.

Country	Feedstocks	Target Renewable	Ref.
United States	Corn	136 BL of biofuels by 2022	[85]
Brazil	Sugarcane	20% blending ratio of bioethanol with gasoline	[86]
European Union	Wheat, Sugar beets, other grains	10% renewable energy in transport by 2020	[85]
Canada	Corn, wheat, straw	5% ethanol	[87]
China	Corn, cassava, wheat, sweet sorghum	10% ethanol-blended gasoline fuels by 2020	[83]
India	Molasses, sugarcane	20% ethanol blending	[88]
Indonesia	Cassava, sugarcane,	25% blending of bioethanol in gasoline by late 2025,	[89]
Thailand	Sugarcane molasses, cassava	30% share in total energy consumption by 2036	[90]

Table 5

World fusel oil production by country (Million litres).

Country	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019
USA	207	251	264	251	251	271	280	290	299	304	299
Brazil	124	131	105	105	118	117	134	138	133	150	163
European Union	20	23	22	22	26	27	26	26	27	27	27
China	10	10	10	10	13	12	15	16	17	20	17
Canada	5	7	9	8	10	10	8	8	9	9	9
Rest of World	4	19	14	14	24	28	22	25	27	30	35
World	384	441	423	412	467	465	485	502	511	540	550

**Fig. 1.** Geographical distribution of major fusel oil end-users.

fuel has a negative affect. It is generally accepted that The formation of NO_x emission is mainly influenced by combustion physics and chemistry [99]. In general, NO_x formation decreased when fusel oil was used compared to pure gasoline. For instance, Icingur and Calam tested exhaust emissions from an SI engine fueled with fusel oil. The authors indicated that NO_x emissions decreased by increasing fusel oil concentration compared with gasoline fuel. Similar trends were observed by Calam et al. [64] and Solmaz [58]. Solmaz stated that incomplete combustion of the fusel oil/gasoline blend caused a significant reduction in NO_x formation by ~31% [58]. Similarly, Awad et al. [96] observed a decrease in NO_x formation when using fusel oil. They explained the decreased NO_x emission in the case of fusel oil by the higher water content of fusel oil. The same work by Simsek and Ozdalyan [97] also observed that NO_x emission decreased with fusel oil usage, whereas increasing the engine load increased in-cylinder temperatures, which also results in higher NO_x formation. The highest

value of NO_x reduction (83.04%) was achieved with fusel oil concentration of 50%. Exhaust analysis also performed by Safieddin et al. [98] who used various blends of fusel oil with gasoline indicated that fusel oil produced fewer NO_x emissions (up to 41%) than gasoline due to lower combustion temperature as a result of water content in the fusel oil (Fig. 3).

4.1.3.2. UHC and CO emissions. The formation of CO emissions has been reported to be linked to many factors, including fusel oil characteristics, type of engine and/or engine working conditions. Moreover, the most critical parameter affecting the CO emissions formation is in-complete combustion. In almost all the published literature, a remarkable increase in the amount of CO emissions was reported when fusel oil was blended with gasoline fuel due to a significant decrease in the temperature of the combustion products. In other words, the energy generated from the combusted fusel oil/

Table 6

Performance and exhaust emission characteristic of SI engines fueled by fusel oil blends in comparison with pure gasoline.

Type of fuel blend	Engine conditions	Performance results				Emission results				Ref.
		BTE	BSFC	Torque	Power	NO _x	CO	UHC	CO ₂	
F10, F20, F30	different speeds/at full load	-	▲	▲	-	▼	▲	▲	-	[49]
F10, F20, F30, F50	different engine load	-	▲	▲	-	▼	▲	▲	-	[64]
F50, F100	different engine load	▼	▲	▼	-	▼	▲	▲	-	[58]
F20, F10	engine speed of 4500 rpm, 60% throttle open position	▲	▲	-	▲	-	-	-	-	[93]
FBWE10, FAWE10	different engine speed, different engine load	▲	▲	-	▲	▲	▼	▼	-	[94]
FBWE10, FAWE10	different engine speed, 45% of WOT	▲	▲	▲	▲	-	-	-	-	[95]
FAWE10, FAWE20	different engine speed, different engine load	▲	▲	-	▲	▼	▲	▲	▲	[96]
F10, F20, F30, F50	different engine load	▲	▲	▲	-	▼	▼	▼	-	[97]
F5, F10, F15, F20	Different load	▼	▲	▼	-	▼	▲	▲	-	[98]

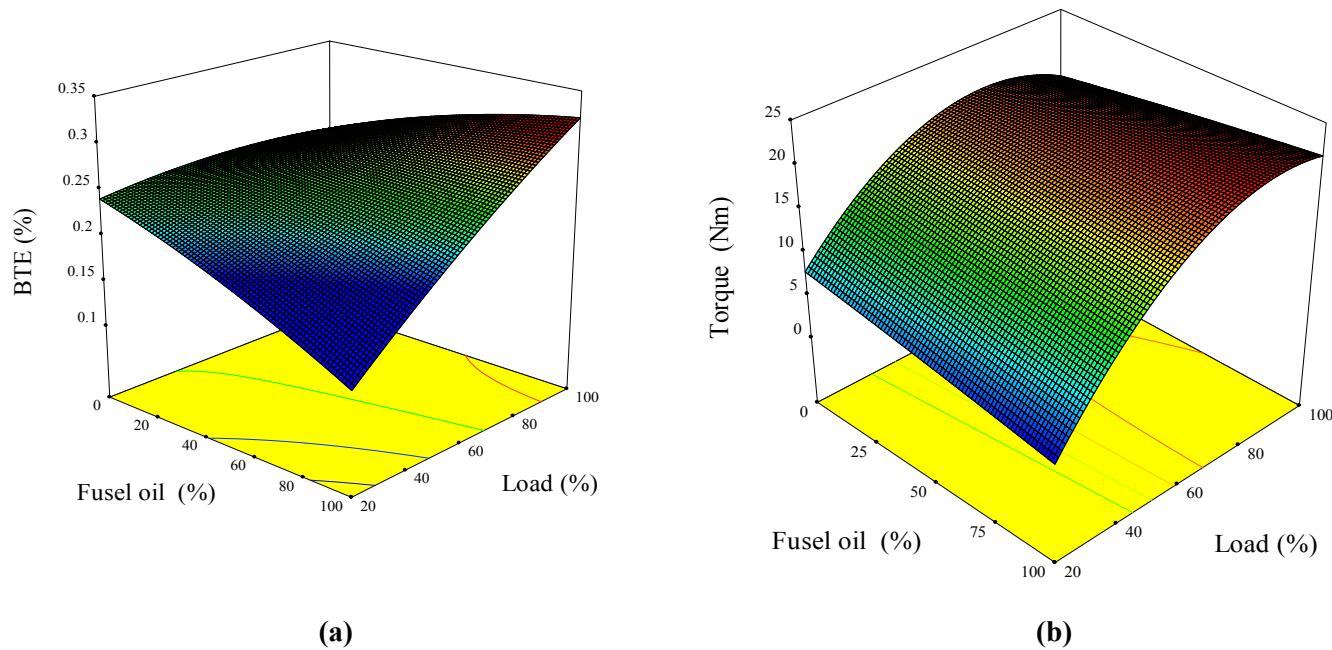


Fig. 2. The interaction effect of fusel oil content and engine load on engine performance [98].

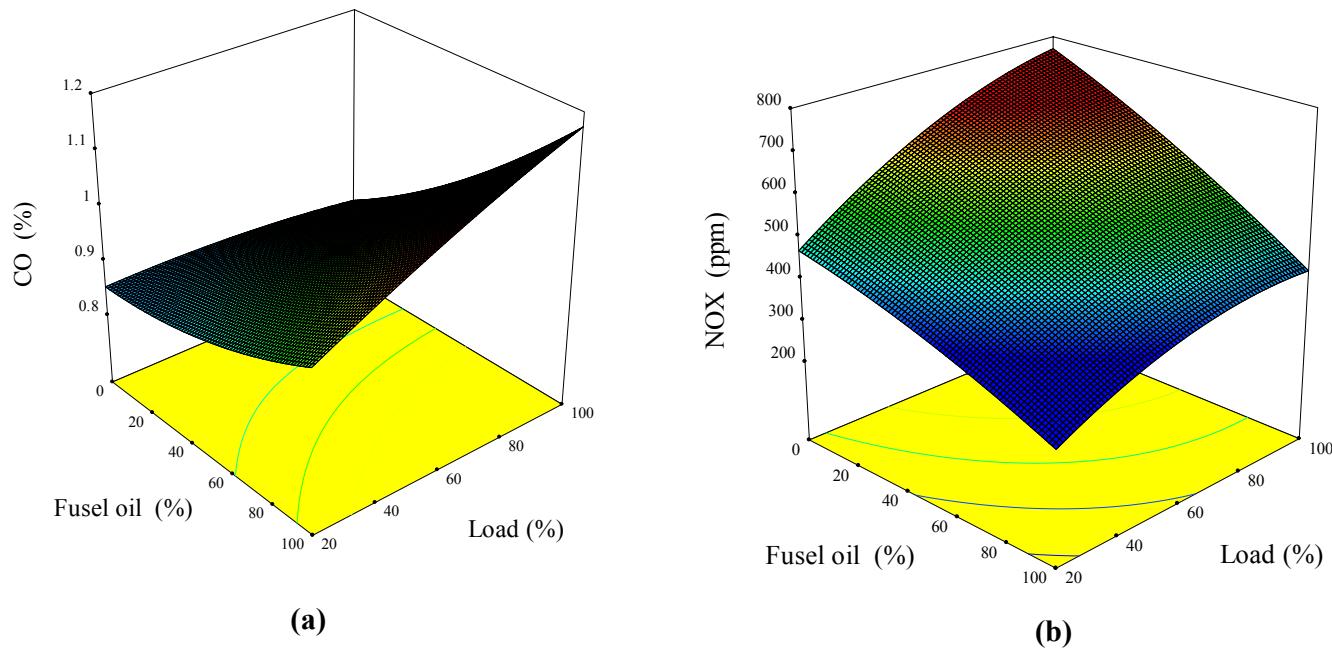


Fig. 3. 3D plots of CO/NO_x emission against different fusel oil content and engine load [98].

gasoline mixture could not provide sufficient heat to transform CO to CO₂. As found by Icingur and Calam [57], fusel oil/gasoline blend increased CO emission were 4.97%, 11.84%, and 14.16% for F10, F20, and F30, respectively. They also observed that as engine speed increased, the CO emission decreased.

Similar results have been confirmed through the experimental study by Solmaz et al. [58], who reported that compared to gasoline fuel, the fusel oil/gasoline mixture led to higher CO emissions (21%) at a speed of 2500 rpm and different engine loads. An increase in CO emissions (9.2%) was also observed by Calam et al. [64] under variable ignition timings. The enhancement trend for the formation of CO emissions was similar to those established by Awad et al. [96]. In a different study, Safieddin Ardebili et al. [98] reported that CO emissions increased by 22% as fusel oil concentration and engine load raised (Fig. 3).

However, in contrast to the above-mentioned reports, Simsek and Ozdalyan [97] argued that the fusel oil/gasoline blends produced significantly lower amounts of CO in comparison with neat gasoline fuel at all engine loads. The authors reported that CO emissions decreased by ~13%, ~26%, ~ 63%, and ~82% for F10, F20, F30, and F50, respectively, compared with gasoline fuel (Fig. 4).

Total UHC emissions were also impacted by fusel oil concentration and engine working conditions. Based on the literature mentioned above, fusel oil usage led to a remarkable decrease in combustion temperature. Consequently, this reduction causes the formation of incomplete combustion products (ICPs) such as UHC and CO emissions increases. Actually, higher CO and UHC emissions is one of the primary challenges in using the blend of fusel oil and gasoline [67].

Icingur and Calam [57] reported that UHC emissions showed a

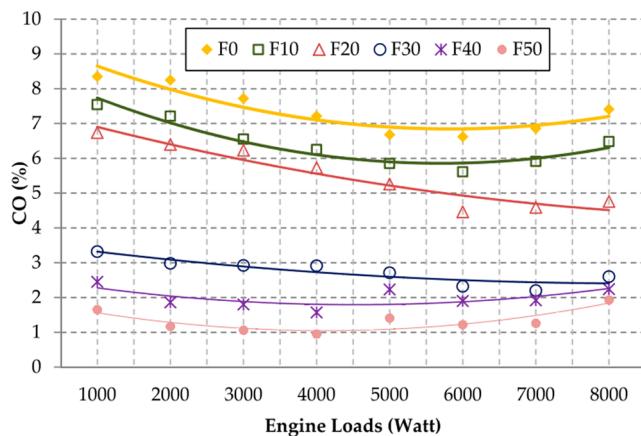


Fig. 4. CO emission variation with different fusel oil ratios and engine loads [97].

significant increase compared to gasoline when fusel oil/gasoline emulsion was utilized. A blend of 30% fusel oil and 70% gasoline led to an increase in UHC emission of 17.6% compared with neat gasoline fusel. They stated that the UHC emissions clearly decreases with the increase of engine speed. Similar results were observed by Solmaz [58]. He found that fusel oil–gasoline blends could increase the UHC emissions up to 25% when using the pure fusel oil fuel. He suggested that the reason to the enhancement of the emitted UHC would be the water content of the fusel oil and ignition timing. In a different study, Awad et al. [96] strived to study the possibility of improving exhaust gas emission of a SI engine fueled with fusel oil/gasoline by extraction of water. They highlighted the improved UHC emissions (~5%) of FAWE10 and FAWE20 compared to FBWE10 and FBWE20 due to increased oxygen- and carbon-content of fusel oil after water extraction (Fig. 5).

Similar results were presented by Safieddin et al. [98], indicating the addition of fusel oil into pure gasoline could enhance UHC emission up to ~29%. The rate of increase of UHC emission at higher level of fusel oil was higher. They attributed their findings to the presence of water in fusel oil and engine working conditions.

Contrary to the above-mentioned investigations in which blending fusel oil with gasoline has been referred for its negative impacts on the UHC emissions, in a study have reported otherwise i.e., reduced UHC emissions by using fusel oil. Simsek and Ozdalyan [97] reported that the addition of fusel oil to gasoline led to significantly decreased UHC production. The amount of UHC emissions was reduced by 50.78%, 45.98%, and 31.81% for F50, F40, and F30, respectively. They attributed this reduction to the oxygen content of the fusel oil and increased in-cylinder temperature.

4.2. Using fusel oil in compression ignition engines

4.2.1. The effect on the engine performance

In the literature, there are research works in which fusel oil has been considered as a green fuel-additive for CI engines, although not as much as SI engines. A number of experimental investigations have been reported on the use of fusel oil as a potential alternative blend component for CI engines. Very few data can be found on the combustion characteristics and performance of a CI engine fuel with fuel oil-diesel blends. Awad et al. were the first to report a series of tests on fusel oil-diesel combustion. The experiment performed by using a YANMAR TF120M single-cylinder diesel engine with a compression ratio (CR) of 17.7:1. The effect of different fusel oil-diesel blends (F0 (pure diesel), F20 (80% vol diesel and 20% vol fusel oil)) at different load levels (50%, 70%) was analyzed. The engine speed levels were 1200, 1500, 1800, 2100, and 2400 rpm. For all the engine loads and speeds tested, they concluded that the cumulative energy release increases were

proportional to the increases in the fuel oil content of the fuel blends [100]. The indicated mean effective pressure (IMEP) model is one of the factors to estimate the indicated torque in internal combustion engines, providing valuable information about the amount of the fuel combustion energy converted into mechanical work. An increase in the fusel oil ratio in the blend slightly decreases in-cylinder pressures when diffusion combustion commences, and ultimately reducing the in-cylinder temperature, as shown in Fig. 6. The observed reduction in in-cylinder pressure, and the temperature is might be attributed to differences in the fuels' moisture/oxygen contents [100]. A similar result was also obtained in a different study conducted by Emiro and Mehmet (2018), who investigated the addition of fusel oil in diesel fuel [101].

Later in a study on diesel-fusel oil fuel blends, Yilmaz [77] confirmed the previous findings but highlighted that at low engine loads, the heat release rate and in-cylinder pressure reduction was intensified with the addition of the fusel oil. This statement is supported by the changing trends in COV_{imep} (%) and in-cylinder pressure data depicted in Fig. 7. More recently, Akcay and Ozer (2019) also observed a similar reduction rate in the in-cylinder pressure with higher ratios of fusel oil in comparison with pure diesel fuel [102]. They stated that the water content in the fuel blends and lower heating value of fusel oil aggravated the combustion process. They found that the remarkable reduction in in-cylinder pressure (10.9%) happened when 20% of fusel oil was added in the diesel fuel [102].

Ağbulut et al. [31] investigated the performance characteristics and emissions of a single-cylinder diesel engine fueled with 10%, 15% and 20% of fusel oil blended in pure diesel and showed slight increases in the maximum heat release rates and the maximum in-cylinder pressure in comparison with neat diesel. They attributed their achievement to the better heat release rate of the blends caused by fusel oil. On the contrary, Yilmaz in their study did not observe any remarkable increase in heat release rate and In-cylinder pressure at all engine loads except at full load as a result of fusel oil addition into diesel fuel. At full load conditions, the IMEP values increased with increasing fusel oil from 5% to 10% [77].

Injection delay is also an important parameter. It is worth quoting that the longer ignition delay of fusel oil results in a comparatively higher heat release rate during combustion [101]. Ağbulut et al. [69] stated that the cetane number occasionally decreased when fusel oil-diesel fuel blends were used, thereby increasing the duration of ignition delay at all engine speeds and loads.

Similarly, Yilmaz (2019) also found that by increasing the fusel oil ratio, the ignition delay increased, as shown in Fig. 8 [77].

Similar findings were also observed by Awad et al. [100], and Akcay and Ozer (2019) [102], where both studies concluded that the low cetane number and high latent heat of vaporization of fusel oil were primarily responsible for ignition delay.

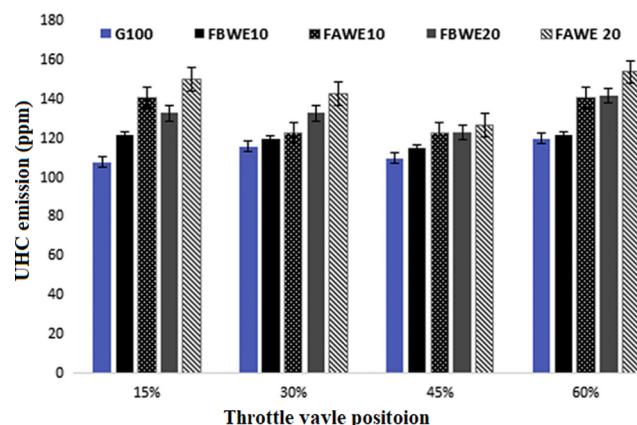


Fig. 5. The effect of fusel oil water extraction and WOT on the UHC emission [96].

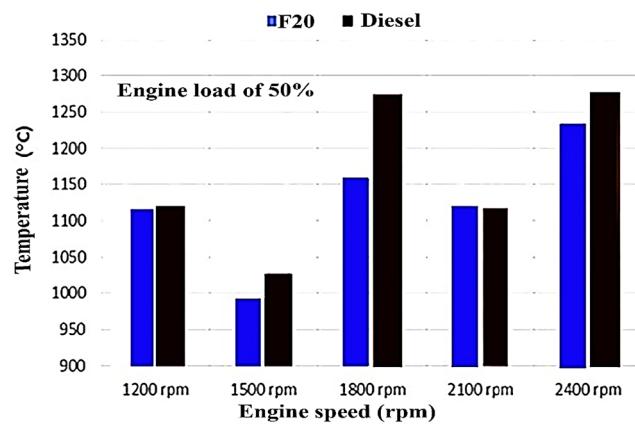


Fig. 6. The variations of in-cylinder temperature at different engine speeds at a fixed load of 50% [100].

The increase in fusel oil quantity (up to 20% by volume) in fusel oil-diesel emulsion is reported to decrease the brake power/torque. Low cetane number and moisture content of fusel oil lead to a slight decrease in the engine power and torque in comparison with pure diesel fuel [100]. Similar results i.e., slight brake power and engine torque reduction at higher blend levels, were reported elsewhere when 5% fusel oil was added into diesel [77] or 20% fusel oil was added into B100 in comparison with neat diesel fuel [72]. Hassan Pour et al. reported a slight increase (5.6%) in engine brake power when fusel oil content increased from 5% to 15%. This improvement could be attributed to the fact that oxygen molecules in the fusel oil could enhance the thermal efficiency of the fuel mixture [58]. Ağbulut et al. [69] reported that the addition of fusel oil to conventional diesel fuel caused a gradual reduction in the brake thermal efficiency (BTE) in comparison with neat diesel fuel.

However, in almost all the published works, the brake specific fuel consumption (BSFC) showed opposite trends with respect to BTE. For instance, Hassan Pour et al. [72] observed that as the fusel oil content in the fuel mixture increased, the BSFC also improved by ~44% over baseline diesel consumption due to a decrease in calorific value of the fuel mixture and an increase in the ignition delay [77]. In addition to biodiesel as an oxygenated additive of diesel fuel, other fuel additives such as nano-biochar derived from sugarcane bagasse have also been used to be a promising solution to improve the engine performance and reduce exhaust emissions. Very recently, Safieddin Ardebili et al. [103] also observed a similar increasing trend in BSFC as a result of the

addition of fusel oil and nano biochar to diesel fuel. They highlight that the use of fusel oil increased BSFC by ~8%, while the engine power decrease by up to ~3%. This improvement in BSFC could also be explained by the low thermal energy of fusel oil [77]. However, at full-load conditions, a slight decrease in engine torque was observed. Overall, the impact of the addition of fusel oil into diesel fuel has been reported to be negative, and BSFC trends demonstrated a local maximum [67,77,104] (Table 7).

4.2.2. Effect on engine emissions

4.2.2.1. NO_x emissions. Several studies have been performed in the literature that were targeted at decreasing NO_x emissions for diesel engines. A review of all of the reported literature up to 2020 revealed a remarkable reduction of up to 25% [100] in NO_x emissions with the use of fusel oil as a fuel additive. For instance, Awad et al. tested fusel oil blended into neat diesel fuel at different engine loads/speeds and recorded an average reduction of 22.5% in NO_x emissions in comparison with diesel fuel. Since the thermal energy of fusel oil is lower than diesel fuel, mixing of fusel oil with diesel fuel can decrease the gas temperature inside the cylinder, thereby reducing NO_x formation. Besides, the water content in fusel oil is mainly corresponding to the reduction of NO_x formation [77].

NO_x formation is highly dependent on the in-cylinder temperature, oxygen concentrations, oxygen concentrations, as well as ignition timing [105–107]. Ağbulut et al. [69] studied the use of fusel oil blends (F0, F5, and F10) in direct diesel engine at full-load operating conditions. He concluded that the NO_x emissions dropped sharply when the fusel oil/diesel mixture changed from 5% to 10%. Minimum NO_x emissions were obtained at a fusel oil concentration of 10% and an engine speed of 2200 rpm.

A similar finding was also observed when referring to the reduction in NO_x emissions when using the fusel oil/biodiesel/diesel blends [72]. Hassan Pour et al. [72] argued that the decrease in NO_x emissions as a result of fusel oil addition is attributed to engine working conditions and the water content of fusel oil. Their findings revealed that NO_x emissions decreased by up to 20%. Furthermore, at low engine loads, NO_x emissions could be reduced [108]. When the engine load increased, NO_x formation significantly tends to increase due to higher exhaust gas temperature in the cylinder chamber and deterioration of fuel atomization [109]. Similar results were obtained by Akcay and Ozer [102], who reported that blending 20% of fusel oil into diesel led to 20% lower NO_x emissions compared to diesel fuel. Similar results were also reported by Safieddin Ardebili et al. [103]. Their results showed a strong correlation between fusel oil content in the blend,

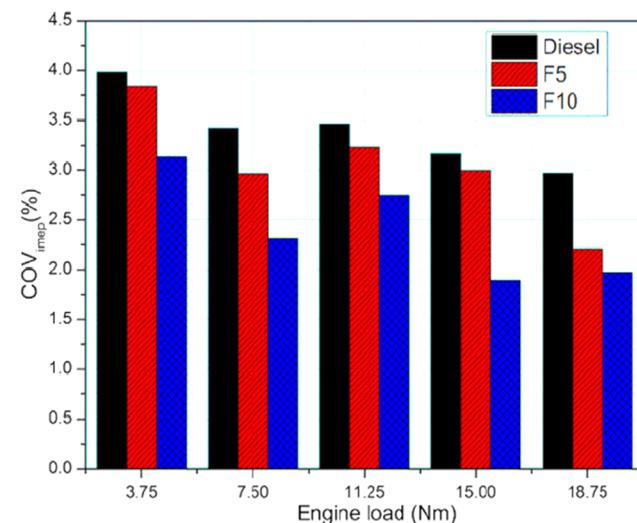
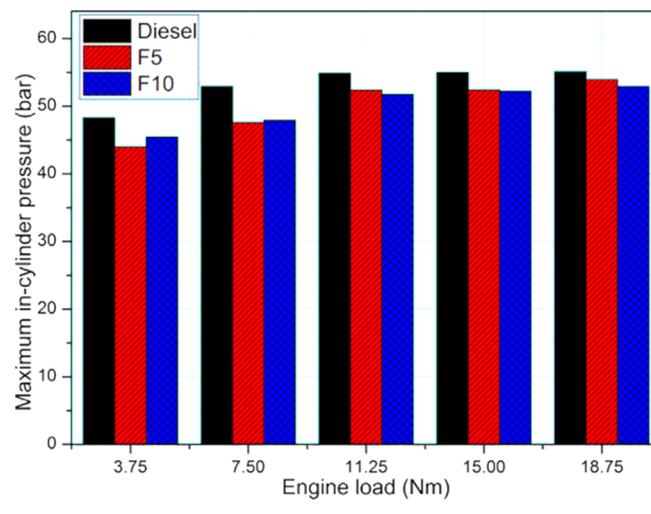


Fig. 7. The effects of different fusel oil-diesel fuel blends on in-cylinder pressure and COV_{imep} (%) [77].

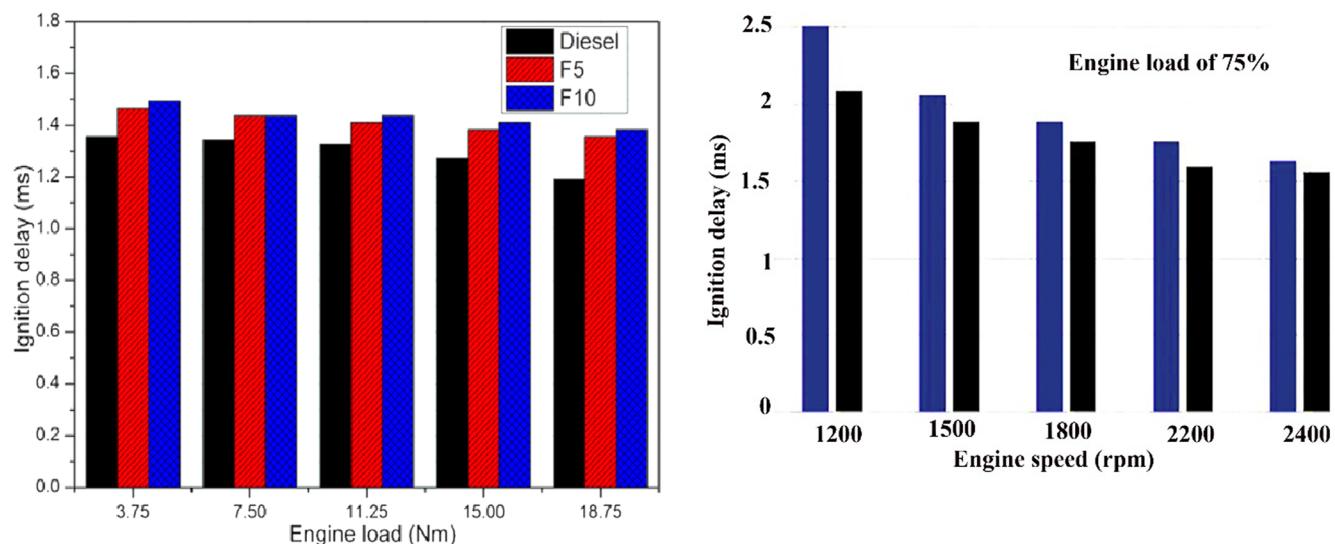


Fig. 8. The effect of fusel oil concentration on ignition delay [77,100].

Table 7

Performance and exhaust emissions of CI engines fueled by different fusel oil blends compared with diesel.

Type of fuel blend	Engine conditions	Performance results				Emission results			Ref.
		BSFC	BTE	Torque	Power	NO _x	CO	UHC	
D80F20	different speeds/loads	▲	-	▼	▼	▼	▲	-	[100]
F5,F10,F15,F20 + biodiesel	different speeds/loads	▲	-	▼	▼	▼	▲	▲	[72]
D95F5, D90F10	different speeds/loads	▲	-	▼	-	▼	▲	-	[77]
F10, F15, F20	different engine loads	▲	▼	-	-	▼	▼	▲	[69]
F5,F10,F15,F20 + biochar	different speeds	▲	-	▲	▲	▼	▲	▼	[103]

engine speed and, nano-biochar concentration in the formation of NO_x. They also reported that the addition of nano-biochar additive into diesel-fusel oil blends significantly decreased the NO_x emissions. They observed a clear decrease in NO_x emissions by 20.51, with increasing fusel oil percentage from 5% to 20%.

4.2.2.2. UHC and CO emissions. Although increasing fusel oil concentration could lead to lower NO_x formation rates, this could result in higher UHC and CO formation rates, due to locally lower temperatures and worse combustion. For instance, Awad et al. [100] studied the addition of F20 into F0. They reported that the engine load of 70%, followed by an engine load of 50%, led to the highest CO emissions in comparison with diesel fuel (20% and 35%, respectively).

Yilmaz [77] showed that the most important issue affecting the formation of CO emission derived from fusel oil combustion was the lower calorific value of fusel oil, which, in turn, led to lower combustion chamber temperature. Hassan Pour et al. [72] also carried out experiments using diesel/ fusel oil/biodiesel combination to achieve the best engine working condition and reported that CO emissions increased by more than 20%. More specifically, they stated that fusel oil is a promising alternative fuel for internal combustion engines due to its origin from a variety of alternative sources. Safieddin Ardebili et al. [103] came to similar conclusions when studying the exhaust emissions of various fusel oil mixtures and bio-based nano additives. They utilized nano-biochar as an additive to reduce the emissions of fusel/diesel blends. However, at higher levels of fusel oil, the in-cylinder temperature decreased sharply, which resulted in higher CO emissions (up to 33%) compared to neat diesel.

In contrast to these reports, Ağbulut et al. [69] reported that the addition of fusel oil (10, 15, and 20%) into F0 decreased the produced CO emissions compared to neat diesel, as shown in Fig. 9.

Similar trends were also observed by Mehmet and Ozer (2019), who

studied the exhaust emission of fusel oil fuel, in which the engine speed fixed at a constant engine speed of 2600 rpm. They indicated that CO emissions reduced by up to 27.7% for all engine loads [102]. Overall, to minimize exhaust gas emissions from CO formation, fuel blends with a low concentration of blended fusel oil and engine speed are preferred.

Most of the efforts have focused on the negative impacts of fusel oil addition on UHC emissions. For instance, Ağbulut et al. [69] reported a significant increase in UHC emissions of 40% with the usage of fusel oil when the engine operated at low loads conditions (Fig. 10). They linked this improvement to the longer ignition delay duration and insufficient oxygen content.

Similar results were reported when Fusel oil/biodiesel additive was added in diesel fuel. Their results showed that UHC emissions increased by 22% for all fuel blends. Safieddin Ardebili et al. [103] studied the effect of five different concentrations of fusel oil/diesel (0, 5, 10, 15, and 20%) on UHC emissions. In contrast to other studies, UHC emissions dramatically decreased by the addition of a nano-biochar additive to fusel/diesel blend up to 14.6%. They claimed that biochar has the

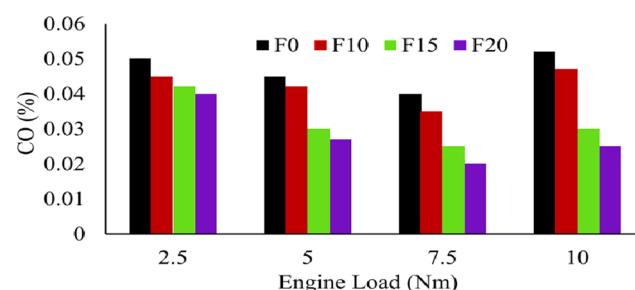


Fig. 9. The effect of fusel oil addition on CO emissions at different engine loads [69].

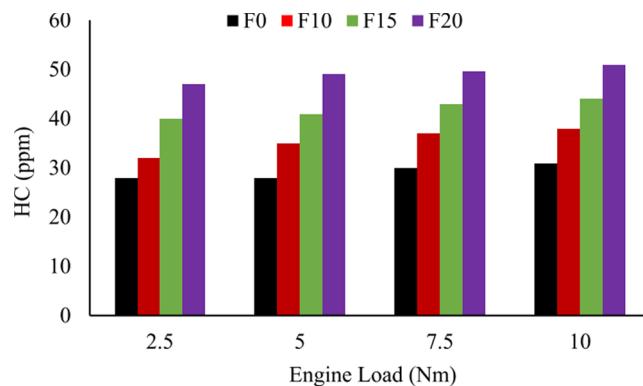


Fig. 10. Variation of UHC emissions versus engine loads at 2000 rpm [69].

potential to improve fusel oil/diesel characteristics and its combustion.

4.3. Fusel oil usage on homogeneous charge compression ignition mode

Homogeneous charge compression ignition (HCCI) combustion, which is presented firstly by Noguchi and Onishi in 1979 [110,111], is a promising technology providing low NOx and soot emissions level simultaneously. The air/fuel mixture is prepared entirely homogeneous as similar as SI engines, and the start of the combustion is obtained by self auto-ignition during compression stroke like CI engines [112–115]. Entirely homogeneous mixture prevents soot formation during combustion. Due to the nature of the HCCI combustion mode, the operational air/fuel ratio is considerably higher than the stoichiometric air/fuel ratio, which means the engine is operated with very lean mixtures. Thanks to the lean mixture, combustion end temperatures are quite low compared to SI and CI combustion modes. As a result of the lower combustion temperatures, NOx emissions are reduced by almost zero. The heat loss from the cylinder walls to the engine coolant also reduces because of the low in-cylinder temperatures. This phenomenon also contributes HCCI engine to provide high thermal efficiency, which is another attractive side of HCCI combustion, even at low compression ratios [116–118]. HCCI studies were commonly carried out by utilizing reference fuels of iso-octane and n-heptan. However, the idea to combine the advantages of biofuels and HCCI combustion mode forced researchers to perform HCCI experiments by using renewable fuels as well [119–122]. Currently, there are three studies available related HCCI combustion utilizing the fusel oil as an energy source [123–125].

4.3.1. Effect of the fusel oil percentage on HCCI combustion

The chemical structure of the fuel is one of the most important parameters affecting the HCCI combustion. HCCI combustion is completely controlled by chemical kinetics. The auto-ignition temperature of the fuel is the main responsible for the start of combustion in HCCI mode. Required heat to increase the fuel temperature is provided by compression during the compression stroke, heat flux from residual gases, and cylinder walls. The research octane number (RON) directly affects the auto-ignition of the air/fuel mixture. The high octane rating of the fuel causes a delay in the start of the combustion and combustion phase [117,118]. The research octane number of fusel oil is about 106, similar to ethanol. It has a considerably high auto-ignition resistance, which is a handicap for HCCI combustion. Therefore, it is very difficult to obtain HCCI combustion by using pure fusel oil, especially at low compression ratios and intake air temperatures. HCCI combustion studies using fuels with high octane number such as ethanol, methanol etc. were conducted by blending these fuels with highly reactive fuels such as n-heptane, diesel etc. [126–129]. A similar approach was used in the fusel oil HCCI studies [123–125].

Calam [124] investigated the effects of the fusel oil percentage in fusel oil/n-heptane fuel blends on HCCI combustion. Three different

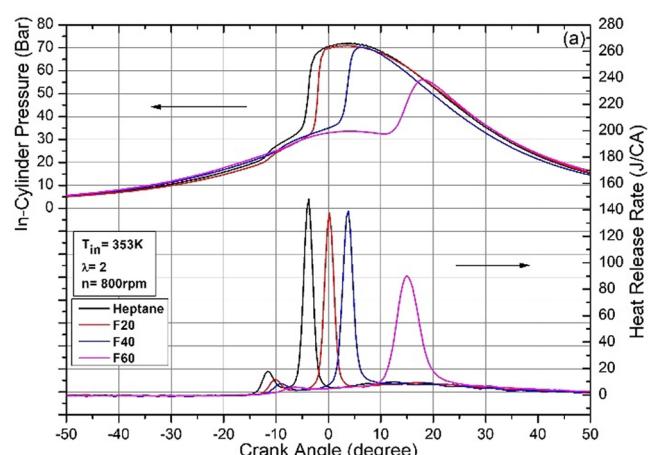


Fig. 11. Effects of the fusel oil percentage on cylinder pressure and heat release rate of HCCI engine [124].

fusel oil/n-heptane fuel blend of F20 (20% fusel oil / 80% n-heptane), F40 (40% fusel oil / 60% n-heptane) and F60 (60% fusel oil / 40% n-heptane) were tested and compared with pure n-heptane operation in this study. In-cylinder pressure traces and heat release rate variations are seen in Fig. 11. Calam reported that the start of the combustion advanced and closed to the n-heptane as the fusel oil percentage decrease in the fuel blend. This case is related to the octane ratings of the blended fuels. The research octane numbers of the F20, F40, and F60 are about 21, 43, and 64, respectively. As is seen on the graph, the combustion started too late with F60 fuel blend. This is an indicator that the engine may not run properly for a wide range. This will also be caused to the engine to be run just in a narrow operation range by means of engine speed and load.

However, the narrowing in operation range is not directly related to the fusel oil or the type of fuel. Fig. 12 will be convenient to explain that in detail. Solmaz [123] conducted a study to compare the performance of the fusel oil in an HCCI engine. In order to perform a suitable evaluation, the results were compared with the experimental test results obtained with reference fuels of iso-octane and n-heptane. Comparison of fusel oil and reference fuels was performed under the same RON of 40. RON40 (40% iso-octane and 60% n-heptane) and Fusel40 (37.5% fusel oil and 62.5% n-heptane) were tested at the same intake air temperature of 350 K. As seen in Fig. 12, the operation range of the engine almost the same in terms of IMEP, engine speed, and load for both types of fuel. Additionally, it was reported that the Fusel40 provided slightly leaner combustion at the misfire region and slightly richer combustion around the knocking region. This means the engine operation range was slightly increased to both high load and low load.

Another comparison study for fusel oil was performed by Calam et al. [125]. In this study, six different fuels ethanol, fusel oil, methanol, butanol, isopropanol, and naptha were compared by blending them with 75% n-heptane. Fig. 13 illustrates a sample of the comparison performed in this study. Sampling fuels from this study were selected as F25 (25% fusel oil and 75% n-heptane) and E25 (25% ethanol and 75% n-heptane) to reveal the performance of fusel oil versus to ethanol. It is clearly seen in Fig. 13 that the operation maps are almost similar to each other. Compared to fusel oil, ethanol just has an advantage in terms of obtained slightly higher IMEP at low engine speeds. Except this, it can be said that both of the fuels performed a similar performance. It is also clear that the heat release and in-cylinder pressure traces are also very similar for F25 and E25 as seen in Fig. 14. The peak pressures and the peak heat release rate values are almost the same, just with an offset in the crank angle. It's seen that the combustion start a couple of crank angle degrees before with F25 fuel compared to E25. It might be caused because of the products in the fusel oil having a lower boiling temperature range. This is another evidence that fusel oil and

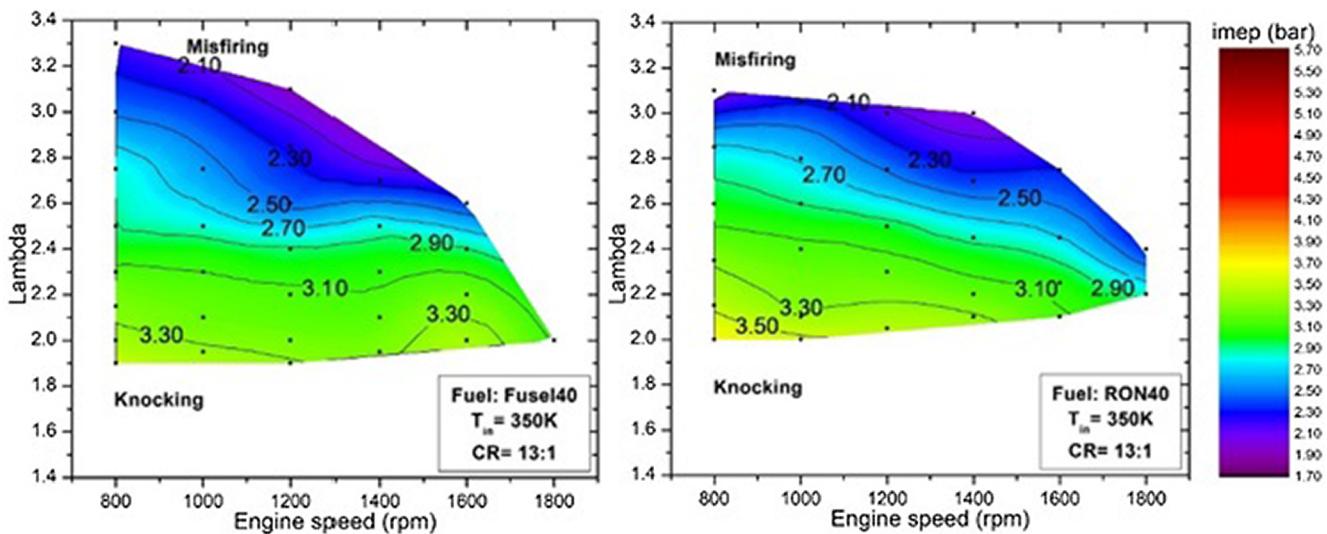


Fig. 12. Comparison of the HCCI engine operation maps for fusel oil/-heptane and isoctane/n-heptane blends at the same RON of 40 [123].

ethanol has very close engine performance, and fusel oil can find more application field.

4.3.2. Effect of the intake temperature and compression ratio

Intake air temperature and compression ratio are critical parameters affecting HCCI combustion and engine performance. Despite there is no direct control mechanism on the start of combustion such as spark ignition, HCCI combustion is directly affected by the intake air temperature and the compression ratio of the engine. An increase in intake air temperature or compression ratio allows the air/fuel mixture to be ignited easier. On the other hand, increasing these parameters too much may cause an increase in the maximum pressure rise rate by advancing the combustion phase before the top dead center. In addition, volumetric efficiency drops with the increase of intake air temperature, and as a result of this, performance loss might have decreased [7,30]. Calam [124] compared the operation maps for F20 (20% fusel oil and 80% n-heptane) at two different intake air temperatures of 373 K and 353 K. It was reported that increased intake air temperature provided a wider operation range for HCCI engine. As seen in Fig. 15, the operation range of the HCCI engine enlarged for both speed range and load range. Another issue about increasing intake air temperature is to providing

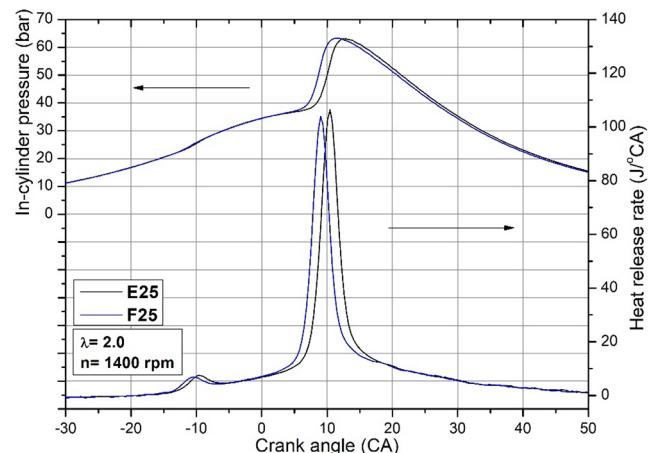


Fig. 14. Comparison of the HCCI engine operation maps for F25 and E25 fuels at the same operation conditions [125].

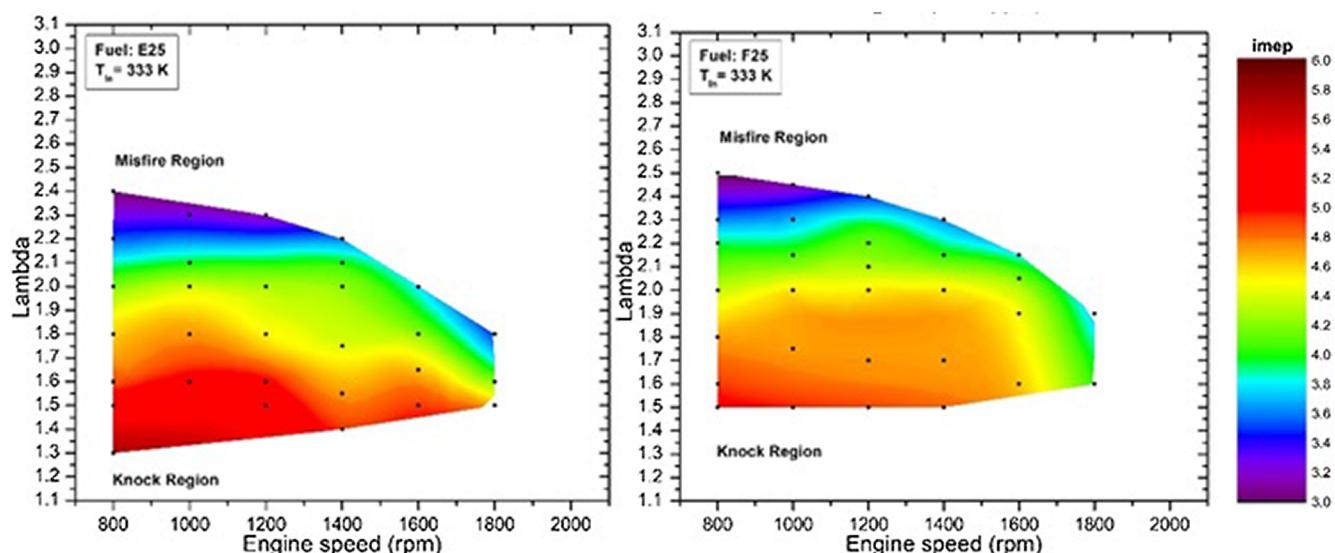


Fig. 13. Comparison of the HCCI engine operation maps for F25 and E25 fuels [125].

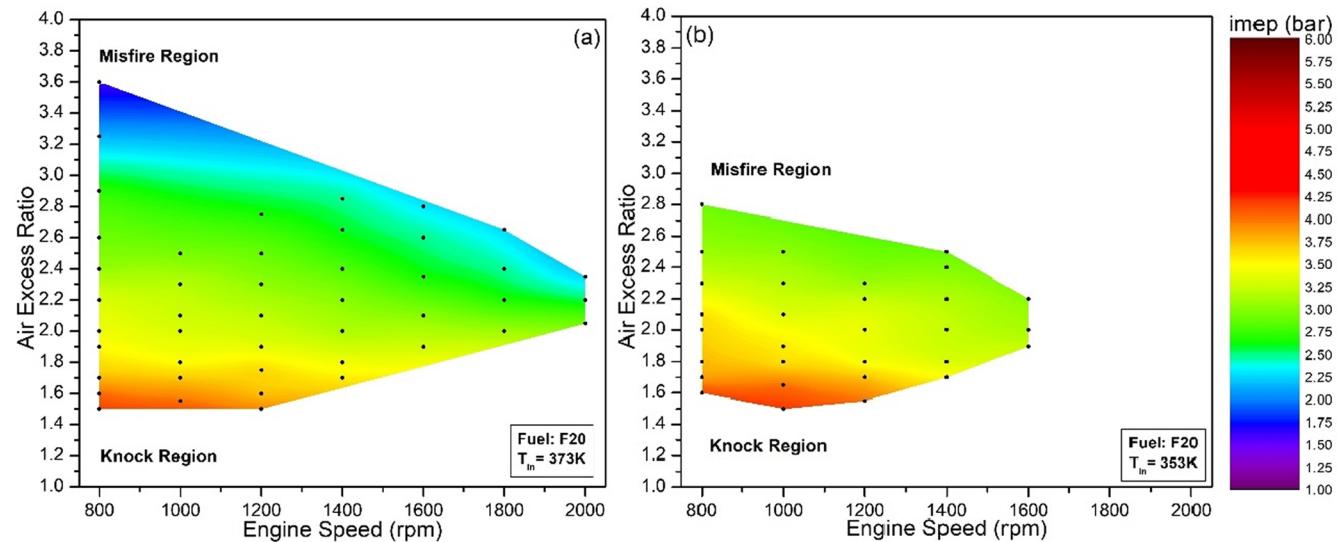


Fig. 15. Comparison of the HCCI engine operation maps for F20 fuel at different intake air temperatures [124].

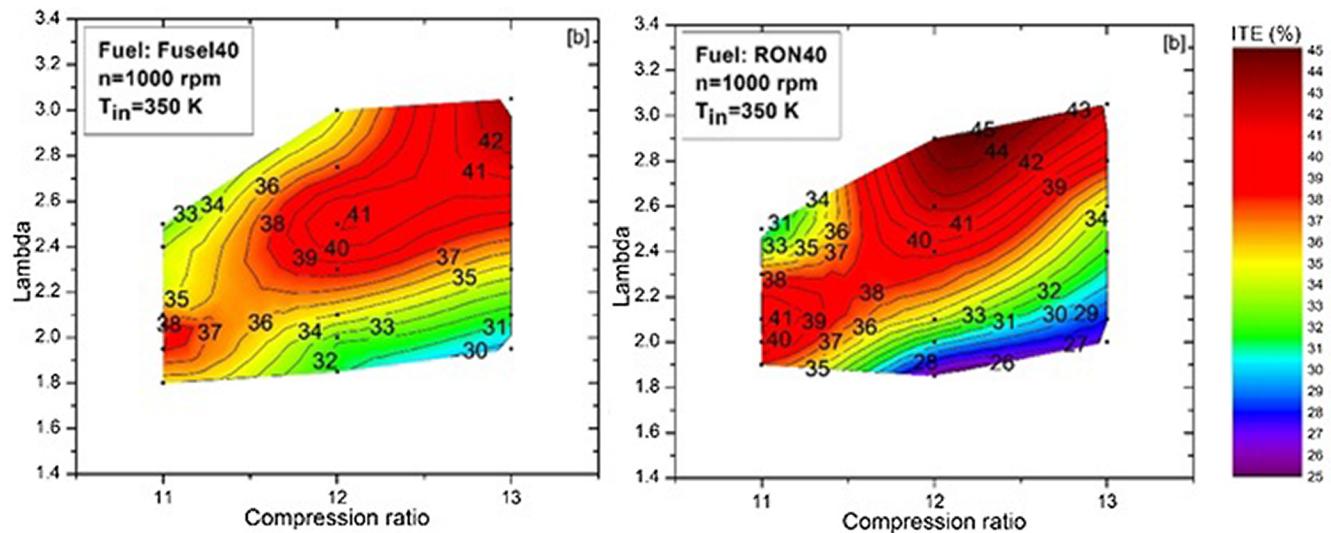


Fig. 16. Comparison of the ITE of HCCI engine for Fusel40 and RON40 fuels at different compression ratios [123].

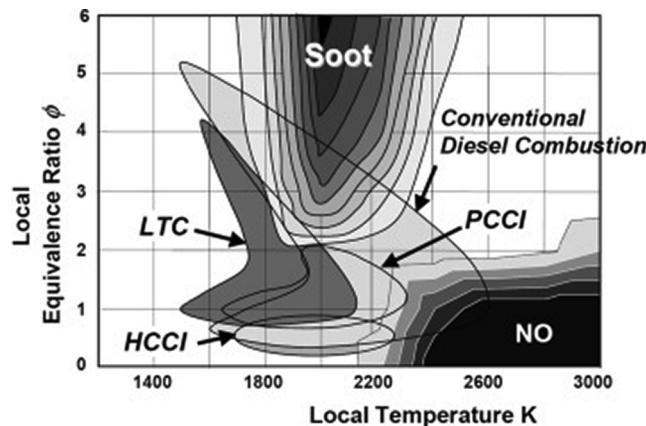


Fig. 17. Emission map of advanced combustion modes on temperature-equivalence ratio domain [137].

energy to heat the intake air. In research studies, the intake air temperature mostly increased by an external heater supplied by electricity. This is not possible for many real-life applications because too much

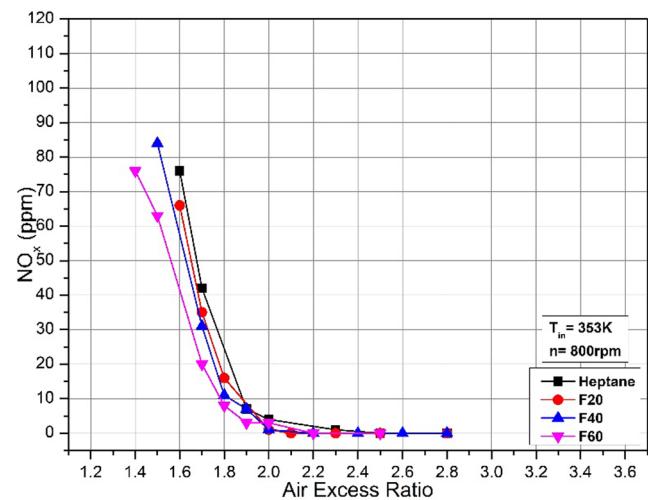


Fig. 18. Variation of NO_x emissions with respect to air excess ratio for fuel oil-heptane blends [124].

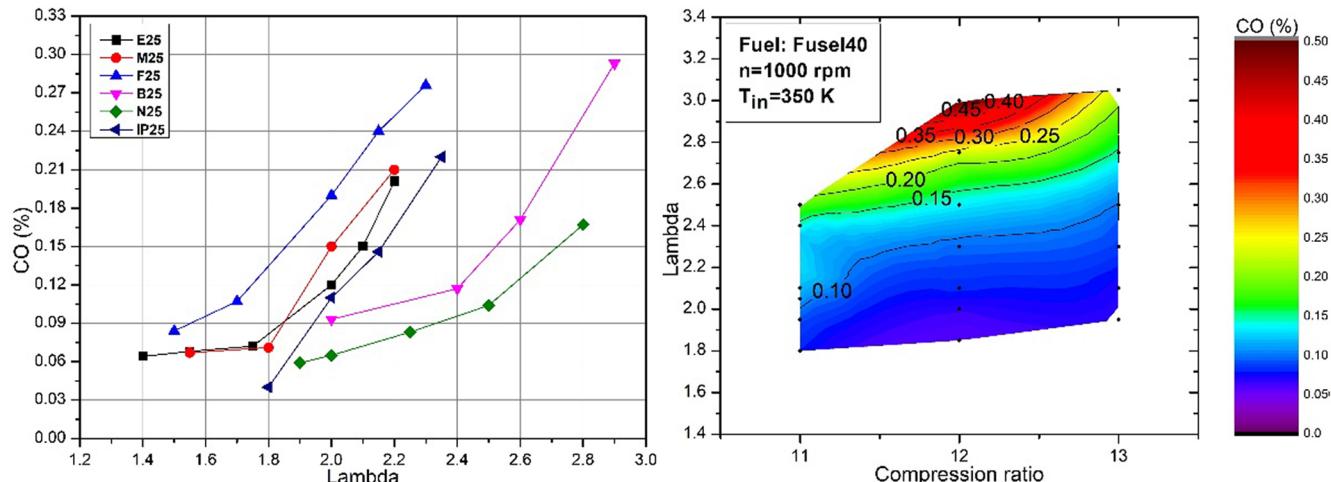


Fig. 19. Variation of CO emissions with respect to air excess ratio for different fuel blends [125] and CO emission map for Fusel40 [123].

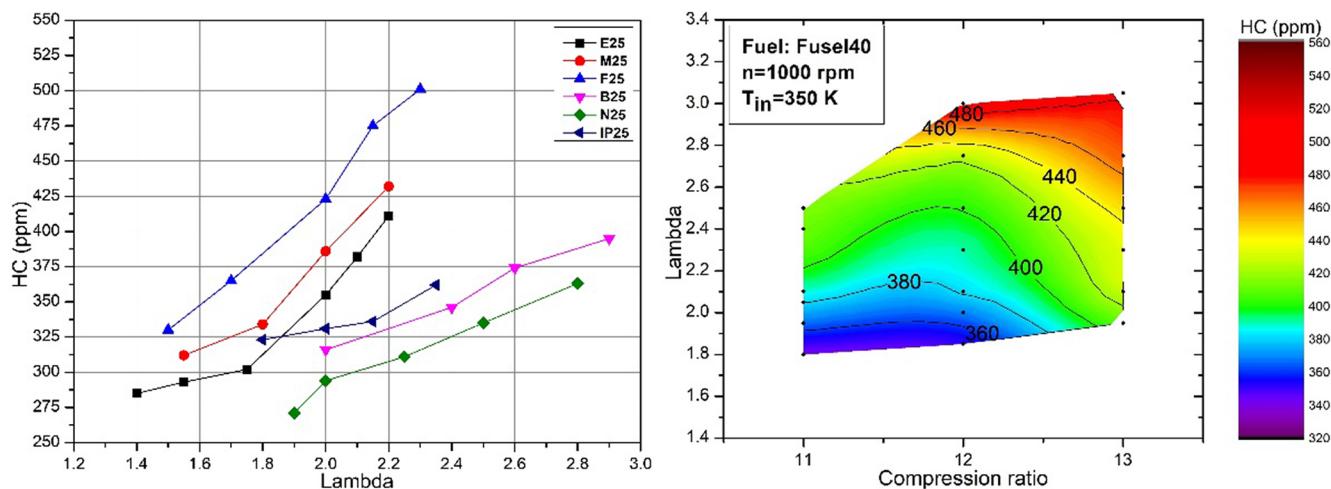


Fig. 20. Variation of HC emissions with respect to air excess ratio for different fuel blends [125] and HC emission map for Fusel40 [123].

energy is required to heat the air, especially for high temperatures. Exhaust waste heat might be a reliable solution to heat the intake air. 353 K is a suitable temperature to obtain with the heat of exhaust gases for HCCI engines. However, 373 K intake air temperature may not be obtained for the whole operation range with the waste heat of exhaust gases because HCCI combustion is low-temperature combustion, and exhaust gas temperature dramatically drops, especially at low loads. Therefore, without energy exergy based analysis, it's so difficult to compare these maps for real-life applications.

Solmaz [123], examined the effects of the compression ratio on HCCI combustion in the use of Fusel40 fuel and compared the results with the RON40. Experiments were conducted on three different compression ratios of 11, 12, and 13. It was reported that the increase in the compression ratio provided both enlarging in the operation range of the engine and a slight decrease in BSFC. Fusel40 and RON40, which RON number of same as 40, were provided nearly the same operation ranges. However, maximum engine torque was slightly higher for Fusel40 thanks to the high latent heat of evaporation that caused a delay on the start of combustion, especially at high compression ratios. Fig. 16 illustrates the comparison of indicated thermal efficiency values for Fusel40 and RON40 at three different compression ratios. At first glance, the red region on the RON map seems to be larger for RON40. However, it can be said that Fusel40 provided higher ITE for a wider range compared to RON40. The ITE values for RON40 are lower than Fusel40, especially at high engine loads. The start of the combustion is advanced at high engine loads because the wall temperatures and

residual gas temperatures increase at high loads. In this case, the advanced start of combustion caused a decrease in IMEP. As a result of this, ITE values may decrease. However, the high latent heat of vaporization of fusel oil prevents the advancing start of combustion to some extent. This result indicates that fusel oil can be used as an alternative to reference fuels. It also may provide higher performance if a variable compression ratio strategy is applied.

4.3.3. Emission characteristics of fusel oil in HCCI mode

Conventional compression ignition engines are preferred for road transportation due to their high energy conversion efficiency compared to spark ignition engines [130]. However, compression ignition engines suffer from NOx and soot emissions [131–133]. Conventional combustion and injection strategies are not sufficient to eliminate NOx and soot emissions simultaneously in compression ignition engines two main stages of combustion [134–136]. In the pre-mixed combustion phase, all of the fuel accumulated in the cylinder during the ignition delay period starts to burn rapidly. Thus, uncontrolled heat release occurs in the cylinder, which increases temperature and pressure remarkably. Excessive in-cylinder temperature triggers NOx formation of the engine working with low equivalence ratios, as seen in Fig. 17. It is possible to reduce the NOx emission by increasing the equivalence ratio that will also resulted an increase in the duration of the diffusion combustion phase. In the diffusion phase, combustion is controlled by the diffusion rate of the fuel injected into the cylinder. Combustion speed depends on the evaporation of the fuel droplets in the spray. In

case of insufficient time to evaporation and mixing with air, liquid fuel droplets in the spray are exposed to thermal cracking because of the high temperature surrounding the spray and soot formation starts. Because of this nature of the conventional diesel combustion, it is not possible to reduce both NOx and soot emissions together. HCCI mode is a combustion mode providing nearly zero soot and NOx emissions like other low temperature combustion modes. The air/fuel mixture is prepared entirely homogeneous in HCCI mode [7,11,135,136]. Besides, a lean mixture provides high oxygen concentration. Thus, the thermal cracking possibility of the fuel is prevented, and soot emissions are completely eliminated in HCCI and other LTC modes. As a result of lean combustion, the in-cylinder temperature does not increase up to NOx formation temperature, so, NOx emissions can also be reduced. However, extremely lean combustion and low combustion temperatures cause an increase in CO and HC emissions. CO results from a lack of oxygen in conventional compression ignition and spark ignition engines [62,113,117]. Although the oxygen concentration is higher in HCCI combustion due to the lean combustion, high CO emissions are observed due to the incomplete combustion. The combustion process is interrupted because of the low in-cylinder gas temperature, which prevents the chemical reactions. Low combustion temperature also causes an increase in HC emissions, especially regions close to the cylinder walls and crevice. However, HC and CO emissions can be reduced by catalytic converter easily if the exhaust gas temperature reaches 250 °C.

Oxygenated fuels such as alcohols, also promote the reduction of the NOx and soot emissions of HCCI engines. The high latent evaporation heat of alcohols reduce the compression end temperatures in the cylinder; thus, peak in-cylinder gas temperatures during combustion decrease. Fig. 18 illustrates the NOx emissions in an HCCI engine operated with fusel oil-n-heptane fuel blends. It is seen that the NOx emission level is quite low compared to compression ignition and spark ignition engines. Calam [124], specified that almost 30 times lower NOx emissions were obtained in HCCI combustion compared to spark ignition mode at an air excess ratio of 1.6. Besides, as the air excess ratio increased, NOx emissions decreased significantly, and almost zero NOx were recorded after air excess ratio of 2. This trend of NOx emissions is related to the decreasing in-cylinder gas temperatures with the increase of air excess ratio. It is also seen that the same air excess coefficients, fusel oil blends provided lower NOx emissions compared to reference fuel of n-heptane. The high latent heat of evaporation of fusel oil causes gas temperatures to decrease. Therefore, fusel oil usage promotes the reduction of NOx like other alcohol-based fuels. There are two other studies about HCCI combustion utilizing fusel oil. Solmaz [123], reported that the NOx emissions were lower than 5 ppm in the use of Fusel40 for all operation range of the HCCI engine. Calam et al. [125] compared fusel oil combustion in an HCCI engine with five different fuels, and in this study, NOx emissions were not reported.

Calam et al. compared fusel oil combustion in an HCCI engine with five different fuel blends. Fig. 19 left graph illustrates the comparison of CO emissions in HCCI engine for the alcohol-based fuels blended with nheptane by volume of 25%. CO emission increases with the air excess ratio due to the decreasing in-cylinder gas temperature. It can also be seen that the CO emissions of F25 fuel are higher than other fuel blends. As it was mentioned before, fusel oil is higher alcohol, and its closed chemical formula is defined as C₅H₁₂O. Its higher carbon number compared to alcohols such as ethanol, methanol, and butanol, causes high CO emissions. The increase in CO emissions occurs not only for HCCI combustion but also spark ignition combustion. Previous studies about fusel oil usage on spark ignition combustion mode demonstrate that fusel oil causes an increase in CO emissions due to its higher carbon concentration [48,58,64,104]. Due to the same reason, fusel oil also causes high HC emissions in both HCCI combustion and spark ignition combustion. As can be seen in Fig. 20 left, higher HC emissions were recorded with F25 fuel blend at all air excess ratios in HCCI combustion. The right side graphs in Fig. 19, and Fig. 20 demonstrate CO and

HC emission maps depending on the lambda and compression ratio for HCCI combustion. It can be said that CO emissions decrease at a high compression ratio thanks to the increased gas temperatures in the cylinder. A decrease in HC emissions is also expected with increasing compression ratio. Crevice regions and wall temperatures are also has a great effect on HC formation. However, lambda is the main parameter determining CO and HC formation in the cylinder, as it is understood from Fig. 19 right, and Fig. 20 right.

5. Conclusions, outlook, and recommendations

Alcohols are promising alternative fuels for internal combustion engines. Higher alcohols having a carbon number of 3 and more are called next-generation alcohols, and their usage in internal combustion engines is investigated by many researchers. Fusel oil, which is a by-product of the fermentation process and abundantly produces over the world during ethanol production especially, consists of mostly higher alcohols. Despite its abundant production rate, fusel oil couldn't find a wide application area to be utilized except for some research studies about the production of biodiesel and bio-lubricant. The idea of fusel oil as a renewable energy source for internal combustion engines was generated in the past decade, and its usability studies in both compression ignition and spark ignition engines was started. In this study, a comprehensive review was conducted to combine the effects of the fusel oil usage in internal combustion engines and present the advantages and limitations of it as an alternative fuel. According to the literature survey, the crucial findings can be listed as below:

1. The high octane number of the fusel oil is a promising feature for spark-ignition engines in particular. Fusel oil-gasoline blends allow the engine to be operated at higher compression ratios. As a result of this energy, the conversion ratio can be increased in real-life applications, and total CO₂ release can be reduced.
2. It was reported that fusel oil has a positive effect on engine torque except two studies. Despite its low lower heating value, the calorific value of the mixture is almost the same compared to gasoline. The oxygenated structure of the fusel oil also heals the combustion. Due to these reasons, the engine torque increased in most of the studies.
3. The raw fusel oil includes water about 5–20% by volume depending on the distillation process and the after storage conditions. The reduction in engine torque can be explained by the water content of the fusel oil.
4. Because of its lower calorific value, fusel oil led to an increase in brake specific fuel consumption for both spark ignition and compression ignition engines. This will cause a reduction in the total drive range for the vehicle with the same storage capacity.
5. Fusel oil seems to be suitable for spark ignition engines due to its alcohol-based properties. Fusel oil provides a proper blend with gasoline without phase separation. However, phase separation occurs in diesel-fusel oil blends, especially higher fusel oil rates after 20%. This might be caused because of several types of alcohols and water in the fusel oil.
6. NOx emissions reduced for both SI and CI engines in case of using fusel oil. The water content of it has a great impact on the reduction in NOx emissions. On the other hand, water cause an increase in incomplete combustion product of CO. For CI engines, fusel provides a simultaneous reduction in NOx and soot emissions thanks to the water content and oxygenated structure. The simultaneous reduction in NOx and soot, is a great achievement because CI engines suffer from these emissions, which are not possible to reduce together.
7. Fusel oil causes higher CO and HC emissions in HCCI mode due to its higher carbon content compared to other alcohol such as ethanol, methanol, and butanol.
8. In HCCI mode, fusel oil has a similar performance with ethanol and reference fuels. Ethanol like features makes fusel oil more attractive.

The results indicated that fusel oil could be used as an alternative fuel in internal combustion engines like ethanol.

The performance loss reported in some of the studies can be eliminated by removing the water from the fusel oil. This will also be helpful to the extent drive range of the vehicles. As it was mentioned before, fusel oil includes several types of alcohols. This structure makes it unstable for different operation conditions. The chemical properties of the fusel oil can be improved by removing some of the worthless types of products. This may allow to increase octane rating and lower heating value of fusel oil together. Fusel oil may also be a proper alternative fuel for homogeneous charged combustion engines. Its less reactive feature may help the control of the start of the combustion and combustion phase, especially for HCCI combustion. The performance of the fusel oil on HCCI mode can be improved further if a variable compression ratio strategy is applied.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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