Alternative fuels for internal combustion engines

A literature review on fuel properties to guide future fuel candidates for internal combustion engines

Jonas Holmborn

Institutionen för Maskinkonstruktion

Skolan för industriell teknik och management

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ICE fuels data summary

Summary

Present report summarizes current sources of fuels, specifications and standards used in vehicle applications. From this start point a survey on published possible future alternative biobased fuels is summarized and data on these fuels are presented in relation to parameters and properties described in current fuel standards. Gaps in fuel data and two proposed research areas in connection to fuel properties are presented.

1. Study on the fuel system interaction with alternative fuels. Fuels considered should include both proposed fuels as neat fuels and as various types of blends. Questions include
   - Filtering of neat/blends fuels
   - Injection pump operation/control
   - Injector operation/control
   - Fuel solution stability and chemical stability within injection systems including high pressures, temperatures and return flow.
   - Fuel deposits formation in tank, filters, pump and injectors. This also includes deposits influence on spray/combustion.
2. Study on the transport system implications from types of alternative fuels. This includes the powertrain as well as the vehicle configuration. Simulation capability for the systems at various levels to be considered.

Sammanfattning

Denna rapport har som ambition att summera nuvarande råvarukällor, specifikationer och standarder för bränslen som används kommersiellt i dagens fordonsapplikationer. Med utgångspunkt från kravställningar och egenskaper hos dagens bränslen har en genomgång vad som publicerats gällande möjliga framtida alternativbränslen gjorts och summerats. Resultaten har sammanställts i form av tabeller där de egenskaper som föreskrivits för dagens bränslen har, efter vad som hittats i litteraturen, visas för de alternativa bränslena. Luckor i publicerade data identifieras och kommenteras till viss del. Vidare föreslås två områden för skapande av forskningsprojekt i relation till bränsleegenskaper:

1. Alternativbränslens interaktion med bränslesystem. Studien bör omfatta både föreslagna kolväten/bränslen i dess rena form samt i olika typer av blandningar. Frågeställningar inkluderar
   ➢ Filtrering av rena- och blandbränslen
   ➢ Drift och kontroll av insprutningspump
   ➢ Drift och kontroll av insprutare
   ➢ Lösnings- och kemiskstabilitet i insprutningssystem, inkluderande höga tryck och temperaturer samt returflöde
   ➢ Reaktionsprodukter och utfällningar från bränslet i tank, filter, pumpar och insprutare. Detta omfattar drivlinan och fordonet. Möjlighet och tillgänglighet till att simulera systemet bränsle-infrastruktur på varierande nivå bör inkluderas.

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Introduction

Liquid fuels have over the past 100 years evolved as the fuels of choice for transport because of their high energy density and the ease of transport, storage and handling. Conventional fuels are complex mixtures that typically contain more than hundred chemical components whose composition has changed and evolved over time and in connection to engine development. The development has been done in correlation with and in order to meet the engine development demand on power, efficiency and drivability. Over the last decades ever more stringent emissions legislations has been added to the demands on the fuel and engine combination. When discussing alternatives to current fossil based fuels for propulsion and power generation fuel properties are important criteria from a combustion point of view to take into consideration, since the combustion behavior relates to the main purpose of the heat machine, i.e., to convert chemical power to mechanical power. However, the fuel in an internal combustion engine undergoes other processes and passes many systems before it is burned, as exemplified in Figure 1, and these also have to be considered. All the systems will influence the fuel and the fuel's different properties will influence the systems.
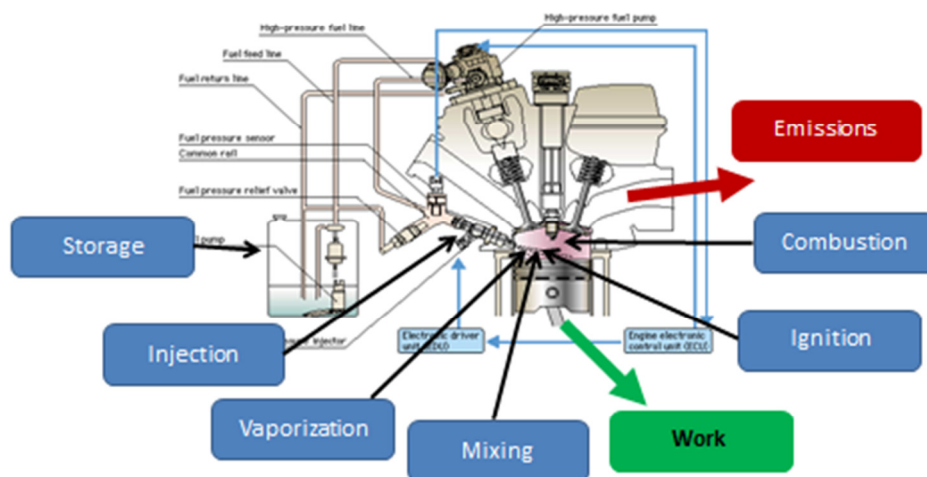
Figure 1 Fuel path through an internal combustion engine (SI example) [courtesy of Martin Tunér]

Fuel is filled and stored in a tank of some type. The fuel will interact with materials and impurities in both storage tank and fuel system. The fuel will also be exposed to various ambient conditions such as temperature, moisture and exposure to oxygen in air. Examples of dependence are vapor pressure, connected to high and low temperatures, deposits depending of low temperature solubility and oxidation stability depending on oxygen content and contact. From the storage, fuel is pumped into the fuel system with feed pumps and pressure pumps, depending on the type of fuel and fuel system. This line also includes various number of filtering stages. All these systems will influence and interact with the fuel when facing material interactions which typically could cause deposits and gum formation. Vapor pressure is also important from a pumping and gas phase formation point of view. Filters are inserted in the line to prevent even very small particles to enter the injectors, but the filters are then very sensitive to clogging due to gum formation or phase separation of components.

Finally fuel enters the injectors where the energy provided by the pressure level is converted into velocity to inject the demanded amount of fuel and, in the case of liquid fuels, to provide energy for spray formation and breakup. The injectors contain small passages and nozzles and also include moving parts which are all very sensitive to clogging and material detoriation. The influence and importance of the fuel's physical and chemical properties in addition to its combustion characteristics are as indicated above covering the whole fuel supply chain from source to end use.

As a result extensive global standards on fuel composition and properties have been built, connected to and supported by a distribution network. [1][2] Details on standards for commercially available fuels can be found in Appendix 1.

When discussing alternatives to present fossil fuels on a large scale the long and often hard learned lessons on the various aspects of the fuel properties inherent in these standards are of vital importance in order not to face problems which are not intuitively found.

Present report aims at presenting an overview of commonly discussed current and future proposed alternative fuels in reflection to the parameters and properties described by the current fuel standards. Since the main source of energy in the combustion of hydrocarbon fuel is the carbon-carbon and carbon-hydrogen bound the variations in theoretically possible hydrocarbon fuels is close to endless. This report will consequently not be able to directly present and comment on all emerging fuels but will rather focus on present and compare most of the types of fuels proposed from a "functional group" or hydrocarbon type perspective. The fuel types are briefly presented in the report text and tables as an overview. For more details and specifications references are made to attach appendixes.

The start point and basis for this presentation and analysis will then have to be the parameters commonly used to describe the fuel's combustion characteristics and fuel specifications and standards which are presented in the following section.

Fuel: sources, description, specifications and standards

Fuel standard specifications are applied to commercially available fuels to assure fit-for-purpose with engine performance and engine durability. Certification fuels (fuels used for engine development, calibration and certification) are typically developed to represent commercially available fuels and for "qualifying" engine/vehicle performance and emissions over representative operating scenarios [3]. Worldwide, fuel specification standards vary by nation and region but most meet or correlate with the standards set by ASTM International [47] or the European Committee for Standardization (CEN) [48].

Standards typically cover four main areas of interest for the engine manufacturers, the society and the customer:

1. Combustion performance (efficiency, power, drivability) and emissions
2. Engine systems influence
3. Transportability (of fuel)
4. Safety and Environmental impact

These parameters are directly or indirectly described, prescribed and validated through the fuels standards, testing methods and guidelines [40-43].

Current European main standards includes the gasoline EN 228, [44] and diesel EN590,[45], both presented in more detail in Appendix 1. Standards for biodiesel EN14214,[46] are in place and are presented in detail in Appendix 2.

Fossil fuel feedstock

Transport fuels are mostly made in refineries starting with petroleum and then blending the products of several refinery processes [3,4]. Petroleum is first separated into different boiling range fractions by distillation. The lightest phase, Liquid petroleum gas or LPG is made up of dissolved gases which are released when the temperature is increased above ambient and might constitute up to 2% of the crude. Its main component is propane in the range of 75%. The fraction boiling in the range from 20°C to 200°C, is termed 'straight run gasoline' (SRG). Products in this boiling range are also termed Naptha and can come from different processes in the refinery. Naphtha has to be processed further to improve its auto ignition resistance before it is used as a gasoline component. The fraction in the boiling range of 160°C to 380°C is termed 'middle distillates'. This fraction includes the commercial Diesel fuel. Depending on the source of the crude, between 40% and 60% of the weight of petroleum can be "Residue" with boiling points above 380 C. These heavier fractions have to be converted through further processing into lighter fractions that can be used as fuel components. A description of refinery and other processes used for making fuel components can be found in Refs. [3,4,5]. Before the various petroleum fractions are used as commercial fuels a number of additives are added to ensure special characteristics of the fuel, apart from the main energy carrying components. These include biofuels as ethanol and other oxygenates such as MTBE (Methyl Tert-Butyl Ether) for gasoline and FAME, HVO (Hydrotrated Vegetable Oil) for diesel. Also bio-based Fischer-Tropsch components and fuels exist but are not commercially available at a significant level. Research is performed on and pilot plants are started and depending on fuel stock and market these components might rise in fraction due to its appealing and tunable characteristics. More details about biofuels can be found in Appendix 2.

Fuel – combustion chemistry, influence and indicators

Fuel's combustion characteristics are mainly classified by their auto ignition quality which is measured by the research and motor octane numbers, RON and MON, for gasolines. Diesels are characterized by the cetane number, CN. The higher the RON, the more resistant is the gasoline to auto ignition while higher CN indicates that the fuel is more prone to auto ignition - there is an inverse correlation between RON and CN [6]. Gasolines need to be resistant to auto ignition to avoid knock, an abnormal combustion phenomenon which limits SI engine efficiency whereas conventional diesel fuels auto-ignite easily. Gasolines are made up of comparatively lighter hydrocarbons with carbon numbers usually between 4 and 11 while diesels contain heavier, higher boiling-point compounds typically with carbon numbers between 10 and 21. RON and MON are measured in tests run according to the procedures set in [7] and are of fundamental importance to the petroleum industry since fuels manufacture is primarily driven by the need to meet the required standards for gasoline octane quality. The RON test is run in a single-cylinder engine at an engine speed of 600 rpm (revolutions per minute) and an intake temperature of 52°C while the MON test is run at 900 rpm and with a higher intake temperature of 149°C. The octane scale is based on two alkanes, n-heptane and iso-octane. Mixtures of these two primary components are referred to as primary reference fuels

(PRF). The RON or MON is the volume percent of iso-octane in the PRF. A fuel is assigned the RON (or MON) value of the PRF that matches its knock behavior in the RON (or MON) test. Cetane number (CN) of a fuel is measured by comparing its ignition characteristics with reference fuels in a single-cylinder diesel engine [7]. The reference scale is based on normal cetane, nhexadecane, which is defined to have a CN of 100 and heptamethyl nonane, highly branched paraffin which is assigned a CN of 15. More recently, a laboratory test method based on measuring ignition delay has been developed to measure the auto ignition quality of diesel fuels [7]. A derived cetane number, DCN, is calculated from the measured ignition delay. Fuels can be said to be in the diesel auto ignition range if CN >30 and fuels with RON >60 (CN <30) can be considered to be in the gasoline auto ignition range [6]. Practical diesel fuels have CN ranging from 40 to 60 while practical gasolines in most markets have RON between 90 and 100. Jet fuel or kerosene has a lower final boiling point, lower cetane and lower density compared to typical European diesel fuel. [2]

The emergence of low temperature combustion strategies, particularly those implementing various ways of chemical reactivity controlled ignition timing and combustion like Partially Premixed Combustion and especially dual fuel based methods to achieve Reaction Controlled Compression Ignition (RCCI), offers the potential to significantly improve operating efficiency and reduce emissions with minimal after-treatment. For all advanced combustion engine technologies a clear understanding of fuel property influences on combustion behaviors will be important to achieving projected engine performance and emissions. Suggested methods for characterization are described in i.e [36-39].

To achieve the benefits projected by emerging engine technologies, the properties of petroleum-derived fuels themselves must be modified over time, but the effects of blending candidate alternative fuels with these conventional fuels must also be understood [3]. Additionally the properties required for fuels in this type of combustion has to be described in a similar manner as for gasoline (MON, RON and for diesel (CN).

Alternative present and future fuels/sources

The two main renewable alternative fuels widely used for transportation [8] are: ethanol [9], and biodiesel (FAME and HVO) [10,11]. Cellulosic and algal renewable fuels will need to emerge with sufficient economic advantage to accelerate alternative fuel usage, and in a manner that better addresses fuel distribution and storage [8]. One way to address the latter is to produce alternative feedstocks that are composed of fully hydrogenated species similar to those found in petroleum derived fuels [12]. Upgrading will require additional hydrogen, and methods for generating hydrogen without increasing carbon emissions are critical needs for the future.

Non-oxygenated fuel feedstocks that are entirely compatible with petroleum have distinct advantages in terms of product refining, distribution, storage, and global fit-for-purpose usage and certification. Examples of this is the HVO from forest and seed base which several fuel producers use as low grade / drop-in in the fossil based diesels. Hydrotreated renewable diesel derived from algae is also under consideration [13–15]. A variety of oxygenated species have emerged as potential ground transportation fuels/fuel components [16]. In addition to extensive research on alcohols [9] and their blends with petroleum (e.g., [17-19]), other types of oxygenated structures such as ethers [20,21], carbonate esters [22,23] valerates [24,25], ketones [26], furans [27–31], acetates [32,33] and oxygenate mixtures of acetonebutanol-ethanol (ABE) [34,35] have all received interest in the last few

years as ground transportation fuel candidates. These are driven by their use as extenders for fossil fuels, in blends with fossil fuels to reduce emissions or increase octane number, and, more recently, for potentially lower processing and refining losses (through bio-refining methods). [8]

Fuel's data and standards

Following section presents the specified properties where standards for various fuels are present and the current state of properties of possible and proposed future fuels for blends as well as for neat fuels.

For each type there are subgroups depending based on base hydrocarbon and added functional groups. For current commercial fuels the division is made based on the standards, for these a summary of content of the standard is also presented. More details on the standards specification and methods within the standards are found in Appendix 1 and 2. Description of the various alternative fuels presented in Table 1 as well as published details on them are found in Appendicies 2-7, where details on alcohols can be found in Appendix 5, methoxyl derivates in Appendix 6 and exotic esters such as levulinate & furoate in appendix 7.

Table 1 Liquid Fuels described in this report

Fossil	Bio-based			
Diesel (App.1)	Biodiesel (App.2)	Alcohols (App.5)	Oxygenated (App.6/7)	Oxygenated mixtures (App.6)
Gasoline (App.1)	HVO / Farnesane (App.3/ 4)	➢ Methanol	➢ Ethers	➢ AcetoneButanolEthanol
LPG (App.1)		➢ Ethanol	➢ Carbonate esters	
		➢ Propanol	➢ Valerates	
		➢ Butanol	➢ Ketones	
			➢ Furans	
			➢ Acetates	

The usage and variations of possible alternative fuels is vast for the liquid fuels. An enormous amount of different fuel configurations have been tested and used over the year. In the last 20 years climate change in combination with security of supply considerations have increased the attention to alternative fuels and with this the number of possible fuels proposals have exploded. For all fuels to be considered the combustion characteristics are of course of vital importance, this is the main process to be performed. However, the demand on a fuel to be considered an alternative for large scale use also includes the production ways/possibilities, the distribution aspects/storage aspects and implications on/interaction with the engines tank and fuel system. Fuel standards and specifications addresses, to various degrees, the above mentioned considerations. To give an introduction to the complexiness and the current level of information available the, in this report,

considered and found sources of fuel characteristics have been summarized in Table 2 - Table 5. In the tables parameters specified in the European standards for commercial gasoline, diesel, biodiesel/FAME and E85 have been listed. Published parameters for the proposed alternative fuels found in publications been listed in the same way. What is first to be noticed is the number of parameters specified in the standards and that approximately one third of the parameters are connected to the combustion characteristics. The rest of the parameters are mostly connected to storage/oxidation stability of the fuels and parameters connected to the interaction with mechanical components and systems such as pumps, filters and injectors. Next to be noted is that in publications related to propose alternative fuels and fuel blends, most data is published based on the combustion characteristics. In a number of publications, mainly where proposed fuels are intended to be blended with existing fuels, other parameters connected to the fuels standards are presented but the implications on engine systems (apart from combustion system) are rarely discussed. For a large number of fuel types the presented parameters are still very limited. If a fuel is to be intended as a large scale alternative attention to the other parameter areas will have to be made. This might also include additional exploration of the fuels blending properties with existing as well as other alternative fuels, something which is not expressively covered by the existing fuel standards.

Table 2 Summary of fuel characteristics information within current report, commercial fuels

		Diesel EN590		Petrol EN228		FAME 14214		HVO	E85
Heating Value	MJ/kg	40,*9		46,5					
Cetane number		51	–	combustion				>70	-
Cetane index		46	–			51,0	–		-
Research octane number, RON				95	--				95
Motor octane number, MON				85	--				85
Total aromatics	% (m/m)							<1.0	
Polycyclic aromatic hydrocarbons	% (m/m)	–	8					<0.1	
Fatty acid methyl ester (FAME) content	% (V/V)	-	7,0					0	
FAME content	% (m/m)					96,5	–	-	
Viscosity at 40 °C	mm2/s	2,000	5			3,50	5,00	2.00-4.00	
Hydrocarbon type content c, f, - olefins - aromatics	% (V/V)			-- --	18,0 35,0				
Benzene content	% (V/V)			--	1				
Oxygen content	% (m/m)			--	4				30,82
Oxygenates content - methanol - ethanol - iso-propyl alcohol - iso-butyl alcohol - tert-butyl alcohol - ethers (5 or more C atoms) - other oxygenates	% (V/V)			-- -- -- -- -- --	3,0 10,0 12,0 15,0 15,0 22,0 15,0			C1OH - 10 C3OH-C8OH 2,0 ethers 5,2	
Distillation % (V/V) recovered at 250 °C % (V/V) recovered at 350 °C 95 % (V/V) recovered at	% (V/V) % (V/V) °C	85	< 65 360						
Distillation 95% (v/v)	°C							<320	
Final boiling point	°C							<330	
Flash point	°C	Above 55,0	–			101	–	>61	
Density at 15 °C	kg/m3	820	845	720	775	860	900	770.0-790.	760-800

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Table 3 Summary of fuel characteristics information within current report, commercial fuels

		Diesel EN590		Petrol EN228		FAME 14214		HVO	E85
Lead content	mg/l			--	5				
Sulfur content	mg/kg	–	10	--	10	–	10,0	<5.0	10
Manganese content f until 2013–12–31 from 2014 to 01–01 onwards	mg/l	- -	6,0 2,0	-- --	6,0 2,0				
Carbon residue g (on 10 % distillation residue)	% (*m/m*)	–	0,30					<0.10	
Ash content	% (*m/m*)	–	0,010					<0.001	
Sulfated ash content	% (m/m)					–	0,02		
Water content	mg/kg	–	200			–	500	<200	5%
Total contamination	mg/kg	–	24			–	24	<10	
Existent gum content (solvent washed)	mg/100 ml			--	5				
Oxidation stability	g/m3 h	– 20	25 -					<25	
Oxidation stability	minutes			360	--				360
Oxidation stability (at 110 °C)	h					8,0	–		
Copper strip corrosion (3 h at 50 °C)	rating	class 1		class 1		class 1		class 1	class 1
Iodine value	g iodine/100 g					–	120		
Linolenic acid methyl ester	% (m/m)					–	12,0		
Acid value	mg KOH/g					–	0,50		0,005% (acidic acid)
Appearance				clear and bright					
Polyunsaturated (≥ 4 double bonds) methyl esters	% (m/m)					–	1,00		
Methanol content	% (m/m)					–	0,20		
Monoglyceride content	% (m/m)					–	0,70 j		
Diglyceride content	% (m/m)					–	0,20		
Triglyceride content	% (m/m)					–	0,20		
Free glycerol	% (m/m)					–	0,02		
Total glycerol	% (m/m)					–	0,25		
Group I metals (Na+K)	mg/kg					–	5,0 l		
Group II metals (Ca+Mg)	mg/kg					–	5,0		
Phosphorus content	mg/kg					–	4,0 m		
Lubricity HFRR at +60°C								<460-650	
Cloud point and CFPP temperate climate	°C					5	-20	-5 ... -34	
Cloud point and CFPP arctic climate	°C					-20	-44		
Cloud point and CFPP as blend component	°C					16	-10		

Table 4 Summary of fuel characteristics information within current report, proposed alternative

		Farnesene	methanol	ethanol	propanol	butanol	Benzaldeh	Phenyleth	Acethoph	Acetone	Ethyl Levulinate C7H12O3	Butyl Levulinate C9H16O3
Heating Value	MJ/kg	44	22,7	29,7	33,6	36,1	31,8	33,2	33,2	29,6	24,3	27,4
Cetane number		60									<5	14
Cetane index			-	-		-						
Research octane number, RON			136	130	112	96						
Motor octane number, MON			104	96		78						
Total aromatics	% (m/m)											
Polycyclic aromatic hydrocarbons	% (m/m)											
Fatty acid methyl ester (FAME) content	% (V/V)											
FAME content	% (m/m)											
Viscosity at 40 ℃	mm2/s	2,32									1,50 cSt	1,99 Cst
Hydrocarbon type content c, f, - olefins - aromatics	% (V/V)											
Benzene content	% (V/V)											
Oxygen content	% (m/m)		49,93	34,73	26,62	21,59	7,98	7,16	6,12	27,6		
Oxygenates content - methanol - ethanol - iso-propyl alcohol - iso-butyl alcohol - tert-butyl alcohol - ethers (5 or more C atoms) - other oxygenates	% (V/V)											
Distillation % (V/V) recovered at 250 ℃ % (V/V) recovered at 350 ℃ 95 % (V/V) recovered at	% (V/V) % (V/V) ℃ ℃	90										
Distillation 95% (v/v)	℃	245										
Final boiling point	℃	245										
Flash point	℃									17,8	90	110
Density at 15℃	kg/m3						1050	1020	1030	791	1,016	0,974

Table 5 Summary of fuel characteristics information within current report, proposed alternative

		Farnesene	methanol	ethanol	propanol	butanol	Benzaldeh	Phenyleth	Acethoph	Acetone	Ethyl Levulinate C7H12O3	Butyl Levulinate C9H16O3
Lead content	mg/l											
Sulfur content	mg/kg										0,9	0,8
Manganese content f until 2013–12–31 from 2014 to 01–01 onwards	mg/l											
Carbon residue g (on 10 % distillation residue)	% (m/m)											
Ash content	% (m/m)											
Sulfated ash content	% (m/m)											
Water content	mg/kg											
Total contamination	mg/kg											
Existent gum content (solvent washed)	mg/100 ml											
Oxidation stability	g/m3 h											
Oxidation stability	minutes											
Oxidation stability (at 110 °C)	h											
Copper strip corrosion (3 h at 50 °C)	rating											
Iodine value	g iodine/100 g											
Linolenic acid methyl ester	% (m/m)											
Acid value	mg KOH/g										0,7	0,4
Appearance												
Polyunsaturated (≥ 4 double bonds) methyl esters	% (m/m)											
Methanol content	% (m/m)											
Monoglyceride content	% (m/m)											
Diglyceride content	% (m/m)											
Triglyceride content	% (m/m)											
Free glycerol	% (m/m)											
Total glycerol	% (m/m)											
Group I metals (Na+K)	mg/kg											
Group II metals (Ca+Mg)	mg/kg										<7	12
Phosphorus content	mg/kg											
Lubricity HFRR at +60°C											430 µm	310 µm
Cloud point and CFPP temperate climate	°C											
Cloud point and CFPP arctic climate	°C											
Cloud point and CFPP as blend component	°C											

Alternative fuels data center, at the Department of energy in the US, has published a comparison matrix of most commonly discussed alternative fuels and the most relevant information is presented in Table 6.

Table 6 Fuels properties for today's main alternative fuels [49]

	Gaso-line/ E10	Low sulfur Diesel	Biodiesel	Propane (LPG)	Compressed natural gas (CNG)	Liquefied natural gas (LNG)	Ethanol/ E100	Methanol	Hydrogen	Electricity
Chemi-cal stru-cture	C_4 to C_{12} and ethanol ≤10%	C_8 to C_{25}	Methyl esters of C_{12} to C_{22} fatty acids	C_3H_8 majority and C4H10 minority	CH_4 (majority), C_2H_6 and inert gases	CH_4 same as CNG with inert gases <0.5%	CH_3CH_2OH	CH_3OH	H_2	N/A
Feed-stock	Crude Oil	Crude Oil	Fats and oils from soy beans, waste cooking oil, animal fats, and rapeseed.	A by-product of petroleum refining or natural gas processing	Underground reserves and renewable bioga	Underground reserves and renewable biogas	Corn, grains, agricultural waste, cellulose	Natural gas, coal, woody biomass, waste	Natural gas, methanol, electrolysis of water	Coal, nuclear, natural gas, hydro, wind, solar
Gasoline gallon equivalent (GGE)	97% - 100%	1 gallon of diesel has 113% of the energy of one gallon of gasoline.	B100 and B20 have 103% and 109% of the energy in one gallon of gasoline and 93% and 99% of the energy of one gallon of diesel, respectively.	1 gallon of propane has 73% of the energy of one gallon of gasoline.	5.66 and 6.38 pounds of CNG have 100% of the energy of one gallon of gasoline and diesel respectively.	5.38 and 6.06 pounds of LNG have 100% of the energy of one gallon of gasoline and diesel, respectively.	1 gallon of E10 and E85 have 96.7% and 73-83% of the energy of one gallon of gasoline (variation due to ethanol content in E85).	1 gallon of methanol has 49% of the energy of one gallon of gasoline.	1 kg of H_2 has 100% of the energy of one gallon of gasoline.	33.7 kWh has 100% of the energy of one gallon of gasoline.
Energy content (lower heating value)	112,114–116,090 Btu/gal (31,3-32,4 MJ/l)	128,488 Btu/gal (35,8 MJ7l)	119,550 Btu/gal for B100 (33,4 MJ/l)	84,250 Btu/gal (23,5 MJ/l)	20,160 Btu/lb (46,9 MJ/kg)	21,240 Btu/lb (49,4 MJ/kg)	76,330 Btu/gal for E100 (21,3 MJ/l)	57,250 Btu/ga (16,0 MJ/l)l	51,585 Btu/lb (120 MJ/kg)	3,414 Btu/kWh
Energy content (higher heating value)	120,388–124,340 Btu/gal (33,6-334,7 MJ/l)	138,490 Btu/gal (38,6 MJ/l)	127,960 Btu/gal for B100 (35,7 MJ/l)	91,420 Btu/gal (25,5 MJ/l)	22,453 Btu/lb (52,2 MJ/kg)	23,726 Btu/lb (55,2 MJ/kg)	84,530 Btu/gal for E100 (23,6 MJ/l)	65,200 Btu/gal (18,2 MJ/l)	61,013 Btu/lb (142 MJ/kg)	3,414 Btu/kWh
Physical state	Liquid	Liquid	Liquid	Pressurized Liquid	Compressed Gas	Cryogenic Liquid	Liquid	Liquid	Compressed Gas or Liquid	Electricity
Cetane number	N/A	40-55	48-65	N/A	N/A	N/A	0-54	N/A	N/A	N/A
Pump octane number	84-93	N/A	N/A	105	120+	120+	110	112	130+	N/A
Flash point	-45°F (-43 °C)	165 °F (74 °C)	212 to 338 °F (100-170 °C)	-100 to -150 °F (-73- -101 °C)	-300 °F (-184 °C)	-306 °F (-188 °C)	55 °F (13 °C)	52 °F (11 °C)	N/A	N/A
Autoig-nition tempe-rature	495 °F (257 °C)	~600 °F (316 °C)	~300 °F (149 °C)	850 to 950 °F (454-510 °C)	1 004 °F (540 °C)	1 004 °F (540 °C)	793 °F (422 °C)	897 °F (481 °C)	1 050 to 1 080 °F (566-582 °C)	N/A

According to Mauss *et al* [50] general ideas on fuel properties can be described as depending on: (1) functional groups, such as alcohols, esthers, alkanes, etc; (2) the length of the molecule; and (3) the structure of the molecule, such as straight or branched, aromatic structures, double bonds etc. A

comparison on octane numbers (RON), cetane numbers and viscosity connected to the molecule lengths has been presented by Mauss *et al* [50], see Table 7 - Table 9.

Table 7 Octane numbers (RON) for some carbon based fuels of different molecule lengths [50]

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
Alkanes	120	108	105	93	62	25	0	-20		
Alkenes [A]						76	66			
Alcohols [B]	109	109	105	96	85	59				
Aromatic (ring)						101 [C]				90 [D]
Aromatic (Methyl group)							120 [E]	118 [F]		
Ether (centered O)		35		0						

(A) Referring to double bond on the first position. (B) Alcohol group on the first position, e.g., 1-butanol. (C) Benzene. (D) Naphthalene. (E) Toluene. (F) Xylene.

Table 8 Cetane numbers for some carbon based fuels of different molecule lengths [50].

	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}
Methyl esters	33.6	47.2	61.4	67.0	74.5	86.9	
Alkanes [A]	63.8	76.9	87.0	96.3	100	108	112

Table 9 Viscosity expressed as micro Pascal seconds at 20 ^{o}C for some carbon based fuels of different molecule lengths [50].

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{12}
Alkanes					222	320	410	530	710	920	1500
Alcohols	610	1190	1900	2900							
Aromatic (ring)						610 [A]				2400 [B]	
Aromatic (Methyl group)							590 [C]	620 [D]			

(A) Benzene. (B) Naphthalene. (C) Toluene. (D) Xylene.

Mauss *et al* [72] also present a rule of thumb for liquid and solid fuels when it comes to calculate the energy content (in lower heating values - LHV) of a fuel that contains the atoms carbon, hydrogen and oxygen:

Energy content LHV [MJ/kg] = 32.8 x m(C) + 101.6 x m(H) − 9.8 x m(O)

and two examples of using the formula are: (1) n-Heptane = 26.9 + 18.1 − 0.0 = 45 MJ/kg, and (2) n-Hexanol = 23.3 + 14.2 − 1.5 = 36 MJ/kg.

Conclusion and research suggestions on fuel characteristics

The number of publications and projects connected to alternative fuels combustion characteristics is large. But, as far as this report covers, the number of studies of the storage, distribution and handling of the proposed fuels are limited. Also the presented studies on blending properties and interaction (both short and long term) interaction with fuel system are much more limited.

The following research topics have been identified as there is a need for deeper understanding:

1. Study on the fuel system interaction with alternative fuels. Fuels considered should include both proposed fuels as neat fuels and as various types of blends. Questions include
   - Filtering of neat/blends fuels
   - Injection pump operation/control
   - Injector operation/control
   - Fuel solution stability and chemical stability within injection systems including high pressures, temperatures and return flow.
   - Fuel deposits formation in tank, filters, pump and injectors. This also includes deposits influence on spray/combustion.
2. Study on the transport system implications from different types of alternative fuels. This includes the powertrain as well as the vehicle configuration. Simulation capabilities for the systems at various levels need to be considered.

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Appendix 1 Commercial available fuels standards

In this section the standards for vehicle fuels, both fossil- and bio-based, which are commercially available today are presented. The standards are presented as the specified parameters and the limit values for each parameter. Following to this a short description on the relevance and influence from the parameters and applied test methods are presented.

Diesel fuel specification (EN 590)

The diesel fuel specification EN590 is here presented as an example of the properties specified in order to assure the consistency of the fuel to be used in a diesel engine with maintained efficiency, power and mechanical integrity over time. The fuel spec is presented in overview in Table 10 Properties described in EN590 [1]**Error! Reference source not found.**Some short comments and clarification on the use and implication for the various parameters are enclosed, but for a more thorough description reference is made to "Worldwide_Fuel_Charter_5ed_2013" [9].

Table 10 Properties described in EN590 [1]

Property	Unit	Limits	
		Min	Max
Cetane Number	-	51	
Cetane Index	-	46	
Density (@15@°C)	Kg/m3	820	845
PAH	% (m/m)	-	8
Sulfur	mg/kg	-	10
Manganese content	mg/l	-	6,0/2,0
Flash point	°C	> 55,0	-
Carbon residue (10%distillation)	%(m/m)	-	0,30
Ash content	%(m/m)	-	0,010
Water content	mg/kg	-	200
Total contanimation	mg/kg	-	24
Copper strip corrosion (3h at 50°C)	Rating	Class 1	
FAME	% (v/v)	-	7,0
Oxidation stability	g/m3	-	25
	h	20	-
Lubricity	μm	-	460
Viscosity @40°C	mm2/s	2,000	5
Distillation	%(v/v) @250°C	-	<65
	%(v/v) @350°C	85	-
	95% recovered °C	-	350

Cetane Index [EN ISO 4264]

The cetane index or cetane number is used to describe the self ignition tendency of the fuel. ISO 4264:2007 describes a procedure for the calculation of the cetane index of middle-distillate fuels

from petroleum-derived sources. The calculated value is termed the "cetane index by four-variable equation" which throughout the remaining text of ISO 4264:2007, is denoted "cetane index".[9]

Polycyclic Aromatic Hydrocarbons

The polycyclic aromatic hydrocarbons, sometimes referred to as PAH have been found to be precursors and by this contribute to particulate formation. Based on this and the ambition to reduce particulates, as one of the regulated emissions from engines, the PAH content was regulated in the EU fuel specifications in the 1990's. [9]

Sulfur content [ISO 20846:2011]

Sulfur naturally occurs in crude oil. If the sulfur is not removed during the refining process it will remain in the vehicle fuel. Cross-contamination can also occur in the fuel distribution system. In traditional diesel combustion system the sulfur content is of no or little concern, it even helps lubrication of fuel system. In modern diesel engines which includes various emission reduction systems, such as EGR or SCR catalyst, high sulfur content might cause problem with corrosion. In present European standard the sulfur content is limited to <10ppm which poses no problems.

ISO 20846:2011 specifies an ultraviolet fluorescence test method for the determination of the sulfur content of motor gasolines, including those containing up to 2,7 %(m/m) oxygen, and of diesel fuels, including those containing up to 10 % (V/V) fatty acid methylester (FAME), having sulfur contents in the range 3 mg/kg to 500 mg/kg. [9]

Metallic elements

The presence of metallic and metalloid species in automotive fuels is undesirable, except in the form of additives in order to improve specific characteristics of the fuel. Metallic or metalloid elements may derive from the raw product, such as nickel and vanadium in petroleum-based fuel or phosphorus in biodiesel, or they may be introduced during production and storage, such as copper, iron, nickel and zinc in case of petroleum-based fuel and alcohol or sodium and potassium in the case of biodiesel. The most famous additive to (gasoline) fuel is undoubtedly lead, the use of which has been banned or drastically reduced now in many countries of the world. The problems related to the trace element content may be economic, such as fuel degradation and poisoning of automotive catalysts, and/or environmental, such as the emission of metal compounds to the atmosphere. [4]

Flash point

The flash point of a volatile material is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Measuring a flash point requires an ignition source. At the flash point, the vapor may cease to burn when the source of ignition is removed. The flash point is not to be confused with the auto ignition temperature, which does not require an ignition source, or the fire point, the temperature at which the vapor continues to burn after being ignited. Neither the flash point nor the fire point is dependent on the temperature of the ignition source, which is much higher. The flash point is often used as a descriptive characteristic of liquid fuel, and it is also used to help characterize the fire hazards of liquids. "Flash point" refers to both flammable liquids and combustible liquids. There are various standards for defining each term. Liquids with a flash point less than 60.5 or 37.8 °C (140.9 or 100.0 °F) — depending upon the standard being applied — are considered flammable, while liquids with a flash point higher than 60.5 or 37.8 °C are considered combustible. [5]

Carbon residue

The carbon residue of a fuel is the tendency of carbon deposits to form under high temperature in an inert atmosphere. It is known that the correlation between carbon residue and diesel engine performance is poor. However, in the absence of any other parameter, this property is included in fuel specifications, indicating the carbonaceous deposit-forming tendencies of the fuel. Many factors can affect the combustion process in diesel engines, including engine loading, engine tuning and the ignition qualities of the fuel which all have an effect on the deposit tendencies of a particular fuel. The carbon residue value of a fuel depends on the refinery processes employed in its manufacture. For straight run fuels, the value is typically 10 - 12% m/m, while for fuels from secondary refining processing the value depends on the severity of the processes applied. In some areas it can be as high as 20% m/m. [6]

Ash content

Diesel fuel can cause abrasive wear of the fuel system and the piston rings if it is contaminated with abrasive inorganic particles. Fuel injectors and fuel injection pumps are particularly susceptible to wear because the high liquid pressures they generate require extremely close tolerances between parts moving relative to one another. [7]

Water content

Water is the most common form of contamination in diesel fuel. There will always be some measure of water in any diesel fuel; however, the total water content is normally less than 200 ppm and—most of the time—measures less than 100 ppm. At around 150 ppm, a slight haze will start to develop in the fuel. However, with adequate filtration and tank maintenance, the occasional presence of slightly hazy fuel should not cause operational problems. When the dissolved water content in fuel repeatedly measures between 200 ppm and 500 ppm, the fuel should be observed and monitored closely. The effects of high or continuous water contamination can lead to:

• Fuel degradation

• Corrosion of certain fuel-wetted components

• Premature plugging of primary and/or secondary fuel filter units

• Fouling of injector nozzles

• Sticking or seizure of critical components within the fuel injector units

• Microbial growth creating sludge and causing additional corrosion and filter plugging [8]

Copper strip corrosion test [ref ASTM D130-12]

Crude petroleum contains sulfur compounds, most of which are removed during refining. However, of the sulfur compounds remaining in the petroleum product, some can have a corroding action on various metals and this corrosivity is not necessarily related directly to the total sulfur content. The effect can vary according to the chemical types of sulfur compounds present. The copper strip corrosion test is designed to assess the relative degree of corrosivity of a petroleum product.[9]

Oxidation stability [EN ISO 12205, EN15751]

The standards describe procedures for the measurement of inherent stability under accelerated oxidizing conditions. The method provides a basis for the estimation of the storage stability, under

the conditions of this test, of middle-distillate fuels with an initial boiling point above approximately 175 °C and a 90% (V/V) recovery point below 370 °C. Is not applicable to fuels containing residual components, or any significant component from a non-petroleum source.[9]

CFPP Cold filter plugging point

CFPP is the lowest temperature, expressed in degrees Celsius (°C), at which a given volume fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions. CFPP gives an estimate for the lowest temperature that a fuel will give trouble free flow in certain fuel systems. This is important as in cold temperate countries, a high cold filter plugging point will clog up vehicle engines more easily. [2]

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Gasoline fuel specification (EN 228)

The gasoline fuel specification EN228 is here presented as an example of the properties specified in order to assure the consistency of the fuel to be used in a diesel engine with maintained efficiency, power, drivability and mechanical integrity over time. The fuel spec is presented in overview in Table 11. Some short comments and clarification on the use and implication for the various parameters are enclosed, but for a more thorough description reference is made to "Worldwide_Fuel_Charter_5ed_2013" [3].

The European Standard EN 228 Automotive fuels - Unleaded petrol - Requirements and test methods - specifies requirements and test methods for marketed and delivered unleaded petrol. It is applicable to unleaded petrol for use in petrol engine vehicles designed to run on unleaded petrol. This European Standard specifies two types of unleaded petrol: one type with a maximum oxygen content of 3.7 % (m/m) and a maximum ethanol content of 10.0 % (V/V) and one type intended for older vehicles that are not warranted to use unleaded petrol with a high biofuel content, with a maximum oxygen content of 2.7 % (m/m) and a maximum ethanol content of 5.0 % (V/V)

Table 11 Properties described in EN228, type 1 maximum oxygen content of 3.7 % (m/m) and a maximum ethanol content of 10.0 % (V/V) [1]

Property	Unit	Limits	
		Min	Max
RON		95,0	-
MON		85,0	-
Lead	mg/l	-	5,0
Density (@15@°C)	kg/m3	720,0	775,0
Sulfur	mg/kg	-	10,0
Manganese content	mg/l	-	6,0/2,0
Oxidation stability	Minutes	360	-
Existent gum content	Mg/100ml	-	5
Copper strip corrosion	Rating	Class 1	
Apperance		Clear and bright	
Hydrocarbon type content	Olefins %(v/v)	-	18,0
	Aromatics %(v/v)	-	35,0
Benzene content	%(v/v)	-	1,00
Oxygen content	% (m/m)	-	3,7
Oxygenates content	%(v/v)		
	Methanol	-	3,0
	Ethanol	-	10,0
	Iso-propyl alcohol	-	12,0
	Iso-butyl alcohol	-	15,0
	Tert-butyl alcohol	-	15,0
	Ehters (C>5)	-	22,0
	Other oxygenates	-	15,0
Vapour pressure (VP)	kPa varying at 6 classes here indicated max span	45,0	100,0

Short technical description and background to the stated parameters are presented below [3]

Octane number

Octane number is a measure of a gasoline's ability to resist auto-ignition; auto-ignition can cause engine knock, which can severely damage engines. Two laboratory test methods are used to measure octane: one determines the Research Octane Number (RON) and the other determines the Motor Octane Number (MON). RON correlates best with low speed, mild-knocking conditions and MON correlates with high-temperature knocking conditions and with part-throttle operation. RON values are typically higher than MON, and the difference between these values is the sensitivity, which should not exceed 10. In North America, (RON + MON)/2 is typically used to specify the octane rating, while many other markets typically specify RON.

Sulfur

Sulfur naturally occurs in crude oil. If the sulfur is not removed during the refining process it will remain in the vehicle fuel. Cross-contamination also can occur in the fuel distribution system. Sulfur has a significant impact on vehicle emissions by reducing the efficiency of catalysts. Sulfur also adversely affects heated exhaust gas oxygen sensors. Reductions in sulfur will provide immediate reductions of emissions from all catalyst-equipped vehicles on the road.

Lead

Tetra-ethyl lead has been used historically as an inexpensive octane enhancer for gasoline, but it will poison vehicle emission control systems. The lead binds to active sites within the catalyst and oxygen sensor, greatly reducing their effectiveness. The tolerance to lead contamination has steadily declined as catalyst efficiencies and sensors have improved, so even a slight amount of lead in the fuel will irreversibly disable the emission control system. As a result, vehicle hydrocarbon and NOx emissions will increase even when the vehicle returns to using lead-free gasoline. Unleaded gasoline must be available wherever catalyst-equipped vehicles refuel; increasingly, this means every market around the world. A global lead-free market also is essential for public health, given lead's well-known adverse health effects. These concerns have led most countries to require lead-free gasoline; the few that have not yet done so should eliminate the use of this fuel additive as soon as possible.

Manganese (MMT)

Manganese is a key component of methylcyclopentadienyl manganese tricarbonyl (MMT), which also is marketed as an octane-enhancing fuel additive for gasoline. Like lead, manganese in the fuel will irreversibly reduce the efficiency of exhaust emission control systems. Studies have shown that most of the MMT-derived manganese in the fuel remains within the engine, catalyst and exhaust system. The oxidized manganese coats exposed surfaces throughout the system, including spark plugs, oxygen sensors and inside the cells of the catalytic converter. These effects result in higher emissions and lower fuel economy. The effect is irreversible and cumulative.

Oxygenates

Oxygenated organic compounds, such as MtBE and ethanol, often are added to gasoline to increase octane or extend gasoline supplies. Oxygenating the fuel also may affect vehicle emissions (tailpipe, evaporative or both), performance and/or durability. Adding ethanol also affects the distillation of the gasoline blend

Olefines

Olefins are unsaturated hydrocarbons and, in many cases, are also good octane components of gasoline. However, olefins in gasoline can lead to deposit formation and increased emissions of reactive (i.e., ozone-forming) hydrocarbons and toxic compounds. More details on fermentation produced olefins can be found in Appendix 4.

Aromatics

Aromatics are fuel molecules that contain at least one benzene ring. In general, aromatics are good octane components of gasoline and high-energy density fuel molecules. Fuel aromatic content can increase engine deposits and increase tailpipe emissions, including CO_2.

Volatility

Proper volatility of gasoline is critical to the operation of spark ignition engines with respect to both performance and emissions. Volatility may be characterised by various measurements, the most common of which are vapour pressure, distillation and the vapour/liquid ratio. The presence of ethanol or other oxygenates may affect these properties and, as a result, performance, driveability and emissions as well.

Deposit control additives

Combustion of even good quality gasoline can lead to deposit formation. Such deposits will increase engine-out emissions and affect vehicle performance. High quality fuel contains sufficient deposit control additives to reduce deposit formation to acceptable rates.

References

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Liquefied Petroleum Gas, LPG specification (EN 590)

Liquefied Petroleum Gas, LPG, consists of the gaseous components of the crude oil feed mainly propane, butane and heptane. Propylene, butylenes and various other hydrocarbons are usually also present in small concentrations. HD-5 limits the amount of propylene that can be placed in LPG to 5%, and is utilized as an autogas specification. Composition, with larger fraction of longer hydro carbons may vary depending on feed source and region where fuels are distributed. This is reflected in the wide range temperature stipulated for vapor pressure for different grades. A powerful odorant, ethanethiol, is added so that leaks can be detected easily. [1]

Table 12 Properties described in EN589 [2]

Property	Unit	Limits	
		Min	Max
MON		89,0	-
Total dienes content	Mole %	-	0,5
Hydrogen suphide		Negative	
Total sulfur content	mg/kg	-	50
Copper strip corrosion	rating(1 h @ 40°C)	Class 1	
Evaporation residue	mg/kg	-	60
Vapour pressure	kPa(g)	-	1550
Vapour pressure	Min 150kPa(g) @ temp Grade A Grade B Grade C Grade D Grade E		 -10 -5 0 +10 +20
Water content		Pass	
Odour		Unpleasant and distinct at 20% LFL	

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Appendix 2 Biofuels demands, specification and guidelines

As biofuels are of high interest for reasons such as climate change, security of supply and economy the demand for the different fuels is steadily increasing from both governmental and users as passenger and heavy duty vehicles. The switch to bio-based fuels will not be done over a night since it takes time to build up production capacity, which in turn faces challenges such as limited raw material supply, production processes and production sites, read more in [1]. This in reality means that the sources of biomass and the types of fuels will vary depending on legislative, economical, technological and regional variations. Also the fleet of vehicles and engines can't and will not be replaced in one instance but is also a matter of gradual replacement. Fuels which are to be introduced and used at a rate which is to have an impact on the fundamental reasons for introducing biofuels will have to meet the same requirements set for fossil fuels. Also the alternative bio-based fuels will have to have a potential to be blended into existing fuels in order to meet fuel demands, at least in a short term perspective.

For diesel applications Fatty Acid Methyl Esters (biodiesel/FAME) is one type of fuels which is viable and is in spread use today. Other promising renewable fuels for diesel applications comprise Hydrated Vegetable Oil (HVO), Biomass To Liquid (BTL based on Fischer Tropsch synthesis) and Fermentation based fuels like Farnesene.

Spark ignition fuels based on renewable sources, include alcohols (methanol, ethanol, propanol, butanol), derivates of alcohols and different ethers. Many of the spark ignition type fuels are also in various ways used or tested to be used as blend/drop-in fuels in diesel fuel depending on the need for large amounts of fuels in the commercial vehicle applications which tends to use diesel engines.

As mentioned previously the fuel standards for fossil based fuels have evolved over a century and thus contains a large number of, sometimes costly, experiences on how to handle and specify the fuels to assure safe storage and operation. For every suggested or introduced new renewable fuel these standards and the findings behind them has to be taken into consideration.

In the coming sections a number of introduced fuels are presented.

Fatty Acid Methyl Ester (FAME) / Biodiesel

Biodiesel is today widely spread and used as fuel in various ways, starting as a low grade (7%) blend in the standard diesel over high grade blends of 10%, 20% and 30% up to usage as 100% neat fuel.

FAMEs are typically produced by an alkali-catalyzed reaction between fats and methanol in the presence of a base such as sodium hydroxide or sodium methoxide, see Figure 2.

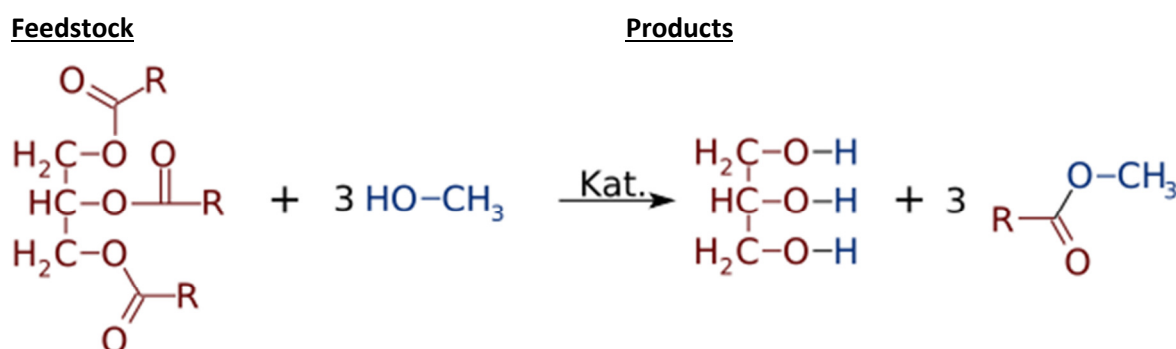**Feedstock**   **Products**

Figure 2 Transesterification FAME [6]

Standards for FAME (neat 100%) are in place within the EN14214 and experiences from the different applications are growing and suggested guidelines on handling, storage and blending are presented in ex WorldWideFuelCharterBiodieselGuidelines.

Since the source for the process are various glycerides and the process does not have a 100% yield presence of unreacted glycerides and methanol is of great importance to the quality of the end product/fuel. The resulting FAME and residual products within are widely varying with the feedstock of the fatty acids. To exemplify, the variations in fatty acid compositions from different feedstocks are presented in Figure 3. Note the difference in the longest C18 acid for commonly used feedstocks such as rapeseed, sunflower seed and palm oil.

Average fatty acid compositions of some vegetable oils and fats [5,56].[a]

Vegetable oil	Palmitic acid	Palmitoleic acid	Stearic acid	Oleic acid	Linoleic acid	Linolenic acid	Others
	C16:0	C16:1(ω7)	C18:0	C18:1(ω9)	C18:2(ω6)	C18:3(ω3)	(C14[b] or $\geq$C20[c])
Cottonseed	28.7	0	0.9	13.0	57.4	0	0
Rapeseed	3.8	0	2.0	62.2	22.0	10.0	0
Safflower seed	7.3	0	1.9	13.6	77.2	0	0
Sunflower seed	6.4	0.1	2.9	17.7	72.9	0	0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0
Palm	43.4	0.3	4.4	40.5	10.1	0.2	1.1[b]
Soybean	11.9	0.3	4.1	23.2	54.2	6.3	0
Tallow	29.5	0.1	19.3	44.4	2.9	0.9	2.9[b]
Jatropha	13.8	0	6.8	41.7	35.6	0.1	2.0[c]
Neem	17.6	0	19.3	55.5	9.0	0	0
Karanja	5.8	0	5.6	71.3	15.0	0	2.3[c]

Extended molecular structures[d]

Figure 3 Fatty acid compositions from various oils [5]

Resulting properties of the FAME fuel compared to standard diesel is presented in Figure 4. Noticeable is the variation in viscosity, pour point and the initial boiling point.

Some fuel properties of methyl esters and diesel fuels

Properties	Methyl esters					Diesel Fuels	
	SFOME	SOME	CROME	COME	CSOME	S.E	N.D
Density (g/cm^3)	0.884	0.885	0.884	0.883	0.884	0.842	0.837
Viscosity (mm^2/s)	4.03	3.97	4.18	4.34	4.06	3.43	2.71
Pour point (°C)	−1	0	−1	−8	6	−6	<−21
Acid value (mg KOH/g)	0.14	0.16	0.17	0.16	0.09	–	–
Ester content (%)	97.1	98.2	97.3	99.2	97.2	–	–
Total glycerin (%)	0.09	0.11	0.17	0.12	0.11	–	–
Free glycerin (%)	0.016	0.020	0.013	0.010	0.019	–	–
Calculated cetane index	60.9	60.1	60.9	61.5	60.3	57.8	55.8
Flash point (°C)	157	139	192	107	149	58	55
Distillation (%)							
IBP	340	338	347	336	344	210	195
10	350	348	350	350	347	239	228
50	352	350	352	352	347	305	283
90	358	357	358	359	359	372	350
EP	384	380	376	382	379	405	372
Recovery	99.0	99.1	99.5	99.5	98.9	95.2	96.5
Residue	0.2	0.2	0.1	0.3	0.3	1.9	1.4
Loss	0.8	0.7	0.4	0.2	0.8	2.9	2.1

SFOME: Sunflower oil methyl ester, SOME: Soybean oil methyl ester, CROME: Corn oil methyl ester.
COME: Canola oil methyl ester, CSOME: Cottonseed oil methyl ester, IBP: Initial boiling point, EP: End point.

Figure 4 properties of biodiesels from various feedstocks [4]

For neat FAME/biodiesel there is a European standard EN14214 in place, see Table 13. The properties specified and levels are to harmonize to the diesel standards, with some variations as for the viscosity, flash point and higher limit of density. A property of the FAME which is not directly specified in the standard, but indicated in the flash point, is the high boiling point of the FAME compared to standard diesel. From a combustion point of view this will influence the spray and to some extent the combustion characteristics, but more importantly the risk of oil dilution is higher

since FAME will accumulate in the lubrication oil where the standard diesel will boil off. Also important to notice is the difference in oxidation stability which is much lower (8 hours) compared to the diesel standard (20 hours). This accentuates the difference in feedstock for the fuel comparing FAME and fossil diesel. The FAME which is based on the esterification of glycerides contains a large number of complex oxygeneated molecules which in their nature are still very reactive compared to the alkanes forming the basis for the fossil fuels. This nature of the fuel requires additional parameters in the specification/standards to control the stability of the FAME. The acid value adds control to the oxidation stability of the fuel, a stable acid value is an indication of the stability of the fuel. Further control of the oxidation stability and tendency to form gums and other sorts of deposits is regulated through the specification of iodine value, indicating the occurrence/number of double bounds in the molecules. The content of the different glycerides/glycerols is also specified and controlled to prevent the formation of gums and deposits.

Table 13 Described properties of FAME (100%) in EN14214 ref [3]

Property	Unit	Limits	
		Min	Max
FAME content	% (m/m)	96,5	-
Density	kg/m3 @40@°C	860	900
Viscosity	mm2/s @40°C	3,50	5,0
Flash point	°C	101	-
Cetane Number	-	51	
Copper strip cor. (3h at 50°C)	Rating	Class 1	
Oxidation stability	h	8	-
Acid value	mg KOH/g	-	0,50
Iodine value	g I/100g	-	120
Linolenic acid methyl ester	% (m/m)	-	12,0
Polyunsaturated (>4 d.b.) methyl esters	% (m/m)	-	1,00
Methanol content	% (m/m)	-	0,20
Monoglyceride content	% (m/m)	-	0,70
Diglyceride content	% (m/m)	-	0,20
Triglyceride content	% (m/m)	-	0,20
Free glycerol	% (m/m)	-	0,02
Total glycerol	% (m/m)	-	0,25
Water content	mg/kg	-	500
Total contanimation	mg/kg	-	24
Sulfated ash content	% (m/m)	-	0,02
Sulfur	mg/kg	-	10
Group I metals (Na+K)	mg/kg	-	5,0
Group II metals (Ca+Mg)	mg/kg	-	5,0
Phosphorus content	mg/kg	-	4,0

Since the nature of the fuel is strongly dependent on the feedstock, which will require various amounts and types of additives to meet specifications, the requirements on temperature stability by cloud point and Cold Filter Plugging Point (CFPP) are specified at different climate zones and grades, see **Error! Reference source not found.** and **Error! Reference source not found.**. The tables, which consists of only the max and min values for the temperate and arctic climate zones, indicates the

large difference in requirements for various zones. Within each climate specification there is a grading, grade A-F in temperate and Class 0-4 in arctic, in which the individual contries which adopts to the standards decides on where to put the demand.

FAME as neat (100%) fuel.

Table 14 CFPP grading for temperate climates, neat FAME [3]

Temperate climates			
Property	**Unit**	**Max, Grade A**	**Min, Grade F**
CFPP	°C, max	+5	-20

Table 15 CFPP grading for arctic climates, neat FAME [3]

Arctic climates			
Property	**Unit**	**Max, Class 0**	**Min, Class 4**
CFPP	°C, max	-20	-44

In the previous discussion on cold temperature stability the fuel at hand was pure (>96.5%) FAME. Most FAME is however used as a drop-in or blend fuel. This application of the fuel again puts specific demands on how to treat the fuel due to its "living" nature. To manage blending of FAME into standard diesel other requirements are set, presented in Table 16 and Table 17.

To be noted the requirements on Cloud point and CFPP seems to be lower, but the specifications are to be set on a national level applying to the regional conditions, and the specification is for FAME before application of any cold flow additives. The blended (diesel and FAME) fuel should also still fulfill the diesel standard.

FAME as blend component in diesel

Table 16 Cold flow properties of FAME as blend component ref [3]

Cold flow property choices			
Property	**Unit**	**Max, Grade A**	**Min, Grade F**
Cloud point	°C, max	16	-3
CFPP	°C, max	+13	-10

Table 17 feedstock residuals specification of FAME as blend component ref [3]

Monoglyceride content choices			
Property	**Unit**	**Max, Grade 1**	**Min, Grade 6**
Monoglyceride	°% (m/m)	0,15	0,70

Biodiesel quality changes over time due to the inherent nature of the fuel. Oxidation reactions begin to affect the fuel as soon as the biodiesel is created. Storage conditions, especially temperature, exposure to water and exposure to oxygen which is naturally present in ambient air, influence the rate of oxidation. Anti-oxidant additives can help slow this degradation process and improve fuel stability up to a point. Depending on the application and climate at application the requirements of

the temperature stability and resulting need/use of stabilizers and antioxidants will vary. Their effectiveness depends on their addition to the biodiesel during or as soon after production as practical. The overuse of anti-oxidants can lead to the additional formation of sludge. Thus, care must be taken in choosing the antioxidant type and amount for maximum effectiveness. It is also critical for biodiesel blendstocks to meet the limits specified in this guidance. After blending, distributors and retailers should avoid storing blends for excessive time periods or under adverse conditions.

References

[1] Heyne S, Grahn M, Sprei F (2015). Systems perspectives on alternative future transportation fuels: a literature review of systems studies and scenarios, challenges and possibilities for bioenergy, production of biofuels and use of alternative transportation fuels. Report within project "A pre-study to prepare for interdisciplinary research on future alternative transportation fuels". CIT Industriell Energi AB and Chalmers University of Technology, Sweden.

[2] WorldWideFuelCharterBiodieselGuidelines (2009)

[3] SS-EN_14214_2012[1]

[4] Alptekin E, et al, " Characterization of the key fuel properties of methyl ester–diesel fuel blends", Fuel 88 (2009) 75–80

[5] L. Coniglio L, et al, "Combustion chemical kinetics of biodiesel and related compounds (methyl and ethyl esters): Experiments and modeling e Advances and future refinements", Progress in Energy and Combustion Science 39 (2013) 340e382

[6] Wikipedia.org

Appendix 3 Hydrotreated Vegetable Oil - HVO

Hydrotreament of hydrocarbons is a process which is known and sometimes used, when needed, in the petrochemical industry producing fossil fuels. The hydrotreating of vegetable oils (HVO) and animal fats are a new application of the general process. It is based on oil refining know-how and is used for the production of biofuels for diesel engines. In the process, hydrogen is used to remove oxygen from the triglyceride vegetable oil molecules and to split the triglyceride into three separate chains thus creating hydrocarbons which are similar to existing diesel fuel components, see Fig 5. [1]
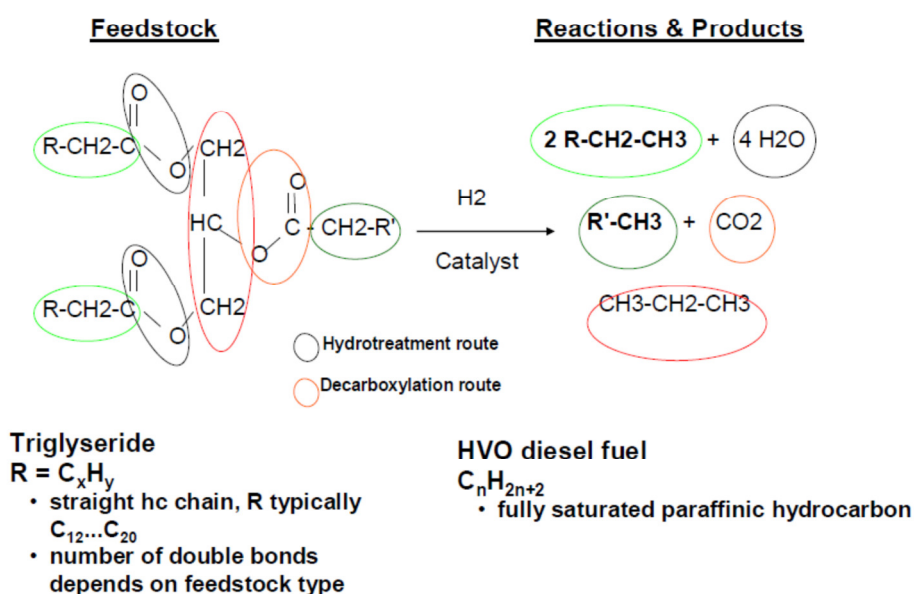
Figure 5 HVO main chemistry - Hydrotreatment and Decarboxylation [1]

The product from the hydrotreament is hydrocarbons where oxygroups and complex branched chains are removed and straight and paraffinic chains are produced. This shift in hydrocarbon structure produces a fuel product which is similar to current diesel fuel, thus allowing seamless blending at any ratio. Typical properties are presented in Figure 6.

Property		HVO (typical NExBTL)	TS 15940:2012 Class A	EN 590:2013
Appearance at +25 °C		Clear & Bright		
Cetane number		> 70.0	≥ 70.0	≥ 51.0
Density at +15 °C	kg/m^3	770.0 … 790.0	765.0 … 800.0	820.0 … 845.0 ≥ 800.0 *
Total aromatics	% (m/m)	< 1.0	≤ 1.0	
Polyaromatics	% (m/m)	< 0.1		≤ 8
Sulfur	mg/kg	< 5.0	≤ 5.0	≤ 10.0
FAME-content	% (V/V)	0	≤ 7.0	≤ 7.0
Flash point	°C	> 61	> 55	> 55
Carbon residue on 10 % distillation	% (m/m)	< 0.10	≤ 0.30	≤ 0.30
Ash	% (m/m)	< 0.001	≤ 0.01	≤ 0.01
Water	mg/kg	< 200	≤ 200	≤ 200
Total contamination	mg/kg	< 10	≤ 24	≤ 24
Copper corrosion		Class 1	Class 1	Class 1
Oxidation stability	g/m^3	< 25	≤ 25	≤ 25
Lubricity HFRR at +60 °C	μm	≤ 460 ** ≈ 650 ***	≤ 460	≤ 460
Viscosity at +40 °C	mm^2/s	2.00 … 4.00	2.00 … 4.50	2.00 … 4.50 ≥ 1.20 *
Distillation 95 % (v/v)	°C	< 320	≤ 360	≤ 360
Final boiling point	°C	< 330		
Cloud point and CFPP ****	°C	As needed -5 … -34	As in EN 590	Down to -34
Antistatic additive		Added		

Data for TS 15940 and EN 590 reproduced with the permission of CEN – © all rights reserved.

*) Winter grades
**) Including lubricity additive when delivered to be used as such in vehicles which are validated for TS 15940 fuel
***) If delivered without lubricity additive to be used as a blending component, preference is to add lubricity additive into the final blend
****) If delivered as such, CFPP is near the cloud point

Figure 6 Properties of pure HVO and relation to fuels standards [1].

Properties like good oxidation stability, cold properties that are similar to standard diesel and high heating values are seen as benefits of HVO compared to biodiesel/FAME. For the injection system, fuel preparation processes and combustion system purposes the similarity of the distillation range/curve, see Figure 7, to the one for diesel is another promising property. Pure HVO has a more defined composition compared to the standard diesel, resulting in a flatter distillation curve. When blended into diesel the distillation curve is almost identical to the standard diesel, resulting in a small need to adopt injection and combustion strategies to the HVO fuel. Adding to the benefits of the boiling point and distillation curve, in comparison to previously discussed FAME, this reduces the risk of oil dilution where problems have been found. This specially relates to engines using particulate filters were thermal management by late injection is applied.
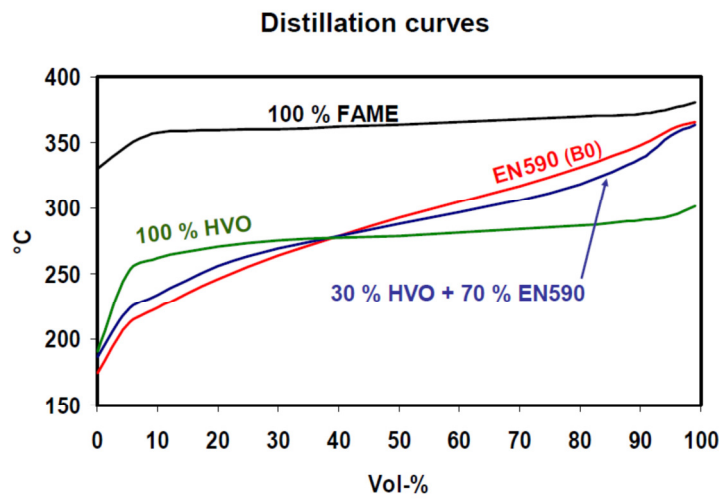
Figure 7 Distillation curve for Diesel, FAME and HVO [1].

References

[1] HVO Handbook Original 2014

Appendix 4 Fermentation produced olefins/alkanes - Farnesene

In the search for alternative hydrocarbon fuels, based on biomass feedstocks, well known and investigated routs are fermentation of sugar or cellulose into alcohols, esterification of vegetable oils into FAME/FAEE or gasification and concurrent synthesis of hydrocarbon molecules. An alternative route, increasingly investigated over the last years [1] [2] [3] is the process of fermentation of sugar or cellulose into straight or branched olefin hydrocarbon chains called farnesenes. The olefin is further treated in a hydration step, removing double bounds, into a branched alkane. These hydrocarbons, with chain lengths of ~C15 show properties directly comparable to diesel, see Figure 8 and Figure 9, without further additives. The resulting product shows promising properties close to standard diesel. Heating value on a mass base in slightly higher compared to diesel, but since density is slightly lower the resulting energy per volume base is slightly lower, but only marginally, than diesel. The viscosity is within the specification range for diesel which promises good operation in pump- and injection system. Boiling and distillation indicates a slightly flatter distillation curve, but not higher final temperature which is important to spray and flame formation. A slightly higher 10% distillation temperature indicates a higher initial boiling point which might influence oil-dilution (compare with FAME). In engine testing, ref [1] and [2] the fuel was tested as blend with diesel and as neat 100% fuel. The results on engine performance were promising with minor effect on efficiency and power, and with reduction of measured emissions. The presented studies on the fuel has to current knowledge been focused on engine operation in controlled conditions while the stability parameters such as oxidations stability and low temperature performance, CFPP and cloud point, are not presented.

Comparison between Sugar cane diesel (Farnesene) vs. commercial diesel fuel (B-S50 - ANP65/2011)		
	Farnesene (100%)	B_S50 (ANP65/2011)
Sulfur content (mg/kg)	0	≤ 50
Density at 20ºC (g/cm³)	0,772	0,820 to 0,850
Cinematic viscosity at 40ºC (mm²/sec)	3,099	2,0 to 5,0
Water (%v)	< 0,05	±0,5
Biodiesel content	0	5
Specific calorific value (MJ/kg)	43,9	42,5
Cetane number	58	min 51

Figure 8 properties of Farnesene and commercial diesel [1]

Fuel Property	DSH	50/50 F76/DSH	F76
Density, 20°C (± 0.2 kg/m^3)	769.4	806.4	841.9
Net Heating Value, 15°C (± 0.8 MJ/L)	34.0	35.3	36.5
Derived Cetane No. (± 1 unitless)	60	56	46
Isentropic Bulk Modulus*, 20°C/0.1MPa (±2 MPa)	1317	1454	1595
Distillation, 10% vol. recover (±2°C)	244	233	217
Distillation, 90% vol. recover (± 1°C)	245	303	316
Kinematic Viscosity, 40°C (±0.01 mm^2/s)	2.32	2.61	2.94
Surface Tension, 21°C (±0.2 mN/m^2)	25.0	26.4	26.9

* Bulk Modulus values calculated from speed of sound measurements

Figure 9 Properties of DSH and diesel [2]

References

[1] Machado, " The Use of Diesel Produced from Sugar Cane at CONAMA PROCONVE P7 Engines, its Environmental Benefits and Influence over the Engine Performance and Exhaust Gas After Treatment System", SAE Tech.paper 2013-36-0209

[2] Hamilton, " Direct Sugar to Hydrocarbon (DSH) Fuel Performance Evaluation in Multiple Diesel Engines", SAE 2014-01-1472

Appendix 5 Alcohol based fuels

Alcohols have been used as an industrial reactant, solvent and fuel for a long time. In the early 1900's both ethanol and methanol were tested and used as a normal fuel for periods. Since the introduction of after-treatment system on gasoline engines in the 1980's with their sensibility to lead and the knowledge on the environmental and health effects from the lead additives in gasoline, alcohols such as ethanol and methanol have been used as a basis for knock preventing additives in gasoline. In this case the alcohols are bases for bio-ethers (e.g., ethanol tertiary butyl ether (ETBE) and tertiary amyl ethyl ether (TAEE). With the increasing demand for alternative and bio-based fuels due to climate and energy sypply concerns the alcohols are gaining ground also as energy carriers, in the form of drop-in/blends in gasoline as well as neat (close to 100%) fuels. Interest is here also shown to higher alcohols such as propanol and butanol, proposals are also found on to use even higher alcohols up to octanol.

Production of alcohols can be done in a multitude of ways, but the most used are based on:

> ➤ Fermentation, which is the classical way of producing ethanol and methanol for food (ethanol) and industrial purposes.
> ➤ Synthesis, by hydration of the alkene
> ➤ Catalytic synthesis, by using syngas (CO and H2) over a suitable catalyst.

Biofuels are of particular interest today due to their potential to help reduce the use of petroleum-based fuels, improve energy security and reduce greenhouse gas emissions. Based on the structures of the biomaterials used and process available (fermentation as well as synthetic catalytic ones), available infrastructure (production and distribution) and combustion properties, various alcohols are being produced already or being evaluated as possible future fuels. [2] [7] See also Table 18-19.

Ethanol is one of these fuels that is viable and in use today as a direct gasoline additive. Other promising renewable blendstocks for gasoline include bio-ethers (e.g., ethanol tertiary butyl ether (ETBE) and tertiary amyl ethyl ether (TAEE)) and bio-alcohols (e.g., biobutanol). Good ethanol quality is fundamental for its continued success as a fuel as well as a feedstock for other fuel additives. [1]

Methanol exists as a base chemical for a variety of different chemical and petrochemical processes in industries besides for fuel production. The alcohol has a long history of usage also as an engine fuel coming back into focus at several occasions over the last century. Methanol is produced in an early stage of various syngas processes and this makes it a promising fuel from an energy efficiency point of view. The alcohol can also be produced efficiently based on fermentation processes.

Propanol and butanol are used as additives in today's gasoline but are also considered as being used as high blends or even neat fuels.

Properties of alcohols in short:

Table 18 Combustion related properties of possible fuel alcohols

Fuel	LHV [MJ/l]	Air-fuel ratio	LHV [MJ/kg]	Heat of vaporization [MJ/kg]	RON-– MON
Methanol	15,9	6.5	20,1	1,16	136 - 104
Ethanol	21,2	9.0	26,8	0,92	130 - 96
Propanol	24,0		29,8	0,73	112-
Butanol	25,9	11.2	32,0	0,56	96 - 78

Table 19 Combustion related properties of pure fuel alcohols [8]

Property	UTG 96	Methanol	Ethanol	Propanol	Butanol	Pentanol
Chemical Formula	C_8H_{15} (Typical)	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH	$C_5H_{11}OH$
Molecular Weight	111.21	32.04	46.07	60.10	74.12	88.15
Oxygen Content, wt. %	0.00	49.93	34.73	26.62	21.59	18.15
Stoichiometric A/F	14.51	6.43	8.94	10.28	11.12	11.68
Specific Gravity	0.7430	0.7913	0.7894	0.8037	0.8097	0.8148
Boiling Point, ^{o}C (^{o}F)	34-207 (94-405)	65 (149)	78.3 (173)	82.2 (180)	82.7 (181)	–
RVP, KPa (psi)	61.4 (8.9)	32.4 (4.7)	19.3 (2.8)	9.0 (1.3)	18.6 (2.7)	–
Net Ht. of Comb., kJ/L (BTU/gal)	31,913 (114,500)	15,887 (57,000)	21,183 (76,000)	23,970 (86,000)	25,921 (93,000)	26,200 (94,000)
Lat. Ht. of Vaporiz., kJ/L (BTU/gal)	223 (800)	920 (3,300)	725 (2,600)	585 (2,100)	474 (1,700)	251 (900)
RON	96.5	112	111	112	113	–
MON	87.2	91	92	–	–	–

Methanol

Methanol, also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits, is a chemical with the formula CH3OH (often abbreviated MeOH). Methanol acquired the name "wood alcohol" because it was once produced chiefly as a byproduct of the destructive distillation of wood. Modern methanol is produced in a catalytic industrial process directly from carbon monoxide, carbon dioxide, and hydrogen.

Methanol is the simplest alcohol, and is a light, volatile, colorless, flammable liquid with a distinctive odor very similar to that of ethanol (drinking alcohol). However, unlike ethanol, methanol is highly toxic and unfit for consumption. At room temperature, it is a polar liquid, and is used as an antifreeze, solvent and fuel. It is also used for producing biodiesel via transesterification reaction. [3]

Ethanol

Ethanol is the alcohol which is most common alternative fuel today. The application spreads from derivates used as additives for gasoline performance purposes, over usage as main fuel as E85 in Europe/US and as pure ethanol fuel in eg Brazil. The combustion and antiknock benefits of ethanol as a neat fuel or as a blending component have been known for a long time. When used as a blending component in gasoline, however, ethanol impacts other fuel properties, especially the vapor pressure and the distillation profile, due to the formation of azeotropes. The spread usage of ethanol as main fuel has demanded the producers of fuel and engines to formulate and agree on standards and specifications to ensure operation and energy content. Ethanol content is included in standard

for gasoline in EN228:2012, please refer to section "gasoline spec" for more details on the specification. This standard allows up to 10 vol% of ethanol and corresponding increase in vapor pressure to allow for the ethanol blend. In Swedish standard EN15938 the use of ethanol as automotive fuel in the E85 application is described, see Table 20. What is different from the gasoline specification is the specifics of water content, which in the ethanol/gasoline mixture becomes important due to the tendency for ethanol to stay mixed with water and then stratify into two one ethanol/water phase and a gasoline phase. The water/ethanol phase will stratify in the bottom of tank and cause deposits. Further the acidity and pH become important to control amounts of oxidation products from ethanol, i.e. acetic acid.

Table 20 Specification on ethanol fuel E85, EN155480

Property	Unit	Limits	
		Min	Max
RON		95,0	-
MON		85,0	-
Density (@15@°C)	kg/m3	760,0	800,0
Sulfur	mg/kg	-	10,0
Sulfats	mg/kg	-	1,7
Oxidation stability	Minutes	360	-
Hartstal	mg/100ml	-	5
Apperance		Clear and bright	
Higher alcohols, C3-C8	Vol%	-	2,0
Methanol	Vol%	-	1,0
Ethers, >C5	Vol%	-	5,2
Water content	m%	-	0,5
Inorganic Cl	mg/kg	-	1,2
pH		6,5	9,0
Copper strip corrosion	Rating	Class 1	
Acidity	m% (as CH3COOH)	-	0,005
Conductivity	µS/cm		1,5

Further details on specifications, mixes, production refer to [1] [5] [6]

Propanol

Propanol is formed naturally in small amounts during many fermentation processes and used as a solvent in the pharmaceutical industry mainly for resins and cellulose esters. Industrial production of propanol is performed by catalytic hydrogenation of Propionaldehyde. 1-propanol has high octane number and it is suitable for internal combustion engine fuel usage. However, production of propanol has been too expensive to be a common fuel. No automotive fuel standards are formulated for propanol.

Butanol

In the strive to increase the amount of bio-based fuels in the current fossil fuels ethanol and methanol has been introduced into gasoline as it blends reasonably and increases octane rating. The solubility and vapor pressure changes connected with ethanol and methanol pose a problem. In this

context the higher alcohol butanol has attracted attention as it has considerable more favorable blending and vapor pressure characteristics.

Butanol is traditionally produced from fossil propene (Shapovalov and Ashkinazi 2008). Butanol isomers can be processed also from biomass. Currently, most biobutanol technologies are based on fermentation, for example, Butamax Advanced Biofuels LLC, Swiss Butalco GmbH, American Gevo Inc. and ButylFuel LLC (2010). Biobutanol can be produced also by catalytic processes (Exelus 2010). Gasification and alcohol synthesis can produce alcohol mixtures, for example Ecalene (Wikipedia 2011).

There are four isomers of butanol with the same chemical formula, but different structural arrangement, see Fig 10. Isomers of butanol are n-butanol, isobutanol, tert-butanol, and sec-butanol. Oxygen contents of butanols are 21.6 wt-%. In past, "gasoline-grade" tert-butanol (GTBA) was commonly present in gasoline as a co-solvent for methanol, denaturant for ethanol and as impurity in MTBE, if produced from TBA. TBA solidifies at about 26°C, and thus co-solvents are needed for handling and usage (API 2001). Today, bio-based isobutanol and n-butanol are considered as blending components for gasoline.

n-Butanol
1-Butanol

Isobutanol

sec-Butanol
2-Butanol
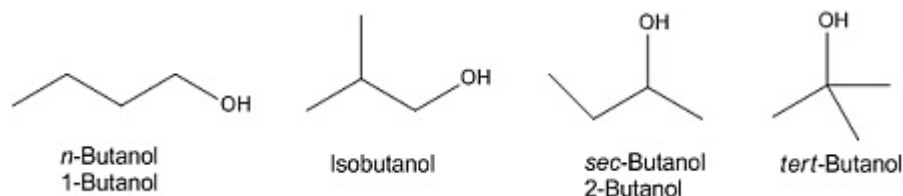
tert-Butanol

Figure 10 Chemical structure of butanol [9]

In Europe, Fuel Quality Directive 2009/30/EC allows maximum 15 vol-% butanol in gasoline. Isobutanol and tert-butanol are mentioned separately, other butanol isomers are covered by the group of "other oxygenates", which means "other monoalcohols and ethers with a final boiling point no higher than stated in EN 228". About 16 vol-% (17 wt-%) of isobutanol would represent gasoline oxygen content of 3.7 wt-%.

Automanufacturer's recommendations for fuel gasoline qualities in the WWFC 2006 edition state that "Higher (C > 2) alcohols are limited to 0.1% maximum by volume." Based on this statement butanol isomers are excluded as gasoline components.

There are no fuel requirements or standards for fuel butanol at the moment. Typical properties of butanol isomers are shown in Figure 11.

	sec-Butanol	tert-Butanol	Isobutanol	n-Butanol
Formula	$C_4H_{10}O$	$C_4H_{10}O$	$C_4H_{10}O$	$C_4H_{10}O$
Molecular weight, g/mol	74.1	74.1	74.1	74.1
Carbon/hydrogen/oxygen, wt-%	64.8/13.6/21.6	64.8/13.6/21.6	64.8/13.6/21.6	64.8/13.6/21.6
Density at 15 °C, kg/dm³	0.806[c]	0.791[d]	0.802[c]	0.810[c]
Boiling point, °C	100[c]	83[a]	108[c]	117[c]
Melting point, °C	-115[c]	25.7[c]	-108[c]	-90[c]
Blending RON *	101[c]	104 – 110[a]	113[c]	94[d], 96[c]
Blending MON *	91[b] (32[c])	89 – 98[a,c]	94[c]	78[c], 81[b]
Neat vapor pressure at 37.8 °C, kPa		12[h]	3.9 (at 40 °C)[i]	2.4 (at 40 °C)[i]
Blending vapor pressure at 37 °C, kPa		62[c]		44[g]
LHV, MJ/kg		33[a]	33[i]	33[g]
LHV, MJ/l		26.1 (calc)	26.5 (calc)	26.7 (calc)
Heat of vaporization, kJ/kg	562[b]	536[b], 601[a]	579[i], 686[c]	584[g], 592[i], 706[c]
Self-ignition temperature, °C	380[b], 406[c]	478[a]	416, 430[c]	343[c]
Ignition limits, fuel in air, vol-%	1.7 – 9.8[c]	2.4 – 8[a]	1.2 – 10.9[c]	1.4 – 11.2[c]
Stoichiometric air to fuel ratio		11.1[a]	11.2[c]	11.2[c]
Solubility in water, 20 °C, wt-%	37[c]	miscible	8.5 wt-%[c,j]	7.7 wt-%[i]
Flash point, °C	31	16	28	34
Viscosity at 20 °C, mPa*s **			3.95[i]	2.9[i]
Viscosity at 20 °C, mm²/s **			4.9 (calc)	3.6 (calc)
Viscosity at 40 °C, mm²/s **			2.7 (calc)	2.3 (calc)
Surface tension at 20 °C, mN/m		20.7[i]	23.0[i]	24.7[i]

*Octane number and vapour pressure of compounds do not behave linearly due to interaction with gasoline components. Blending octane numbers depend on the gasoline composition. ** Kinematic viscosity at 20 °C (cSt = mm²/s) = Dynamic viscosity (cP)/density at 20 °C (kg/dm³) Note: 1 Pa * s = 10 P = 1 cP

[a] Owen 1995 [b] Prezelj 1987 [c] Cooney 2009 [d] BP 2006 [e] Graboski 2000 [f] Rice 1991 [g] Zwaja 2009 [h] Unzelman 1991 [i] BASF Technical leaflets [j] CRC Handbook

Figure 11 Selected properties of butanol isomers

Melting point

Melting point of tert-butanol (TBA) is about 26°C. However, in past TBA was commonly present in gasoline as a co-solvent for methanol, denaturant for ethanol and as impurity in MTBE. Melting points of other butanol isomers are below -90°C.

Octane numbers

Sufficient knocking resistance, octane rating, is essential for proper operation of spark-ignition engine. Octane numbers of methanol and ethanol are high. Blending octane numbers of butanol isomers are somewhat lower than those of ethanol. Of butanol isomers, the highest blending octane numbers are achieved with isobutanol: blending RON 114 and MON 94. For n-butanol, blending MON is as low as 78-81). Figure 12 shows octane numbers of various alcohols. The sensitivity (difference between RON and MON) is typically 8-10 units for gasoline, while over 10 for butanol isomers. Blending MON is particularly low for n-butanol.
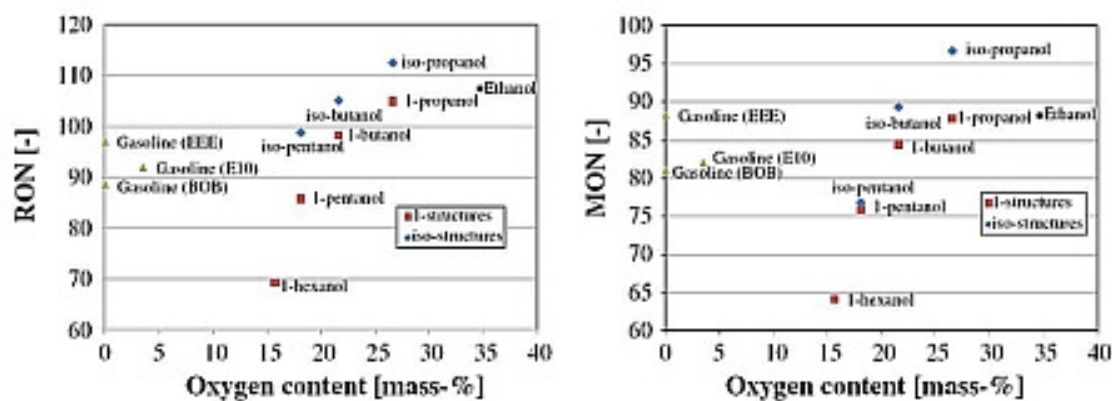
Figure 12 RON and MON octane numbers of various alcohols [11].

Volatility and distillation

Butanol has a lower blending vapor pressure than ethanol. Basically, butanol does not significantly increase vapor pressure of gasoline at any blending ratio, Figure 13.
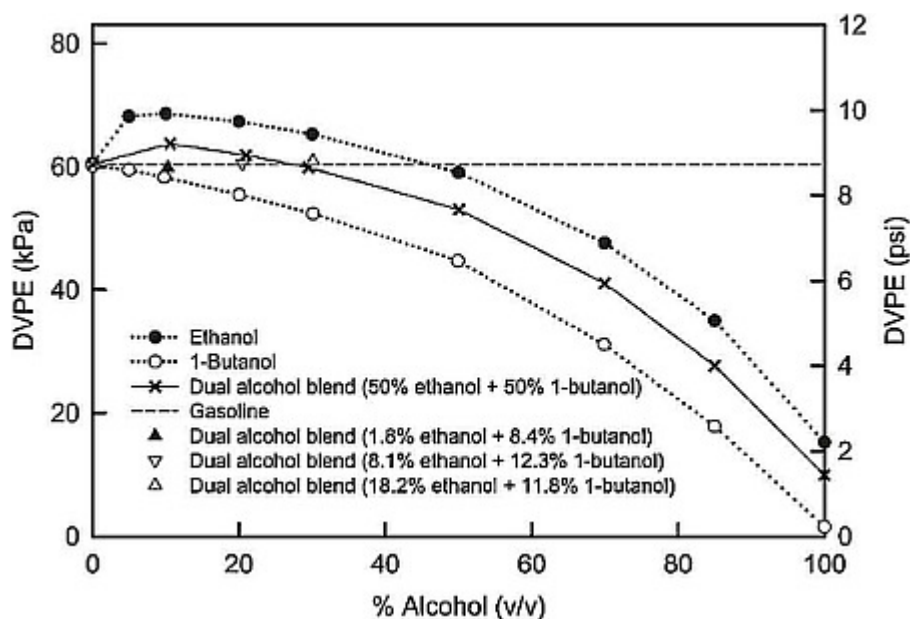

Figure 13 Vapor pressure of gasoline/alcohol mixtures [13]

Boiling point of isobutanol is 108 °C and that of n-butanol is 117 °C. These butanol isomers bring higher boiling components into gasoline than ethanol Figure 14. Mid-range distillation components increase substantially when butanol is blended with gasoline. E100 limit (volume evaporated at 100 °C) of the European gasoline standard (EN228) may need consideration, if butanol is used as gasoline component. Bruno et al. (2009) have reported the effect of all butanol isomers on distillation curves.
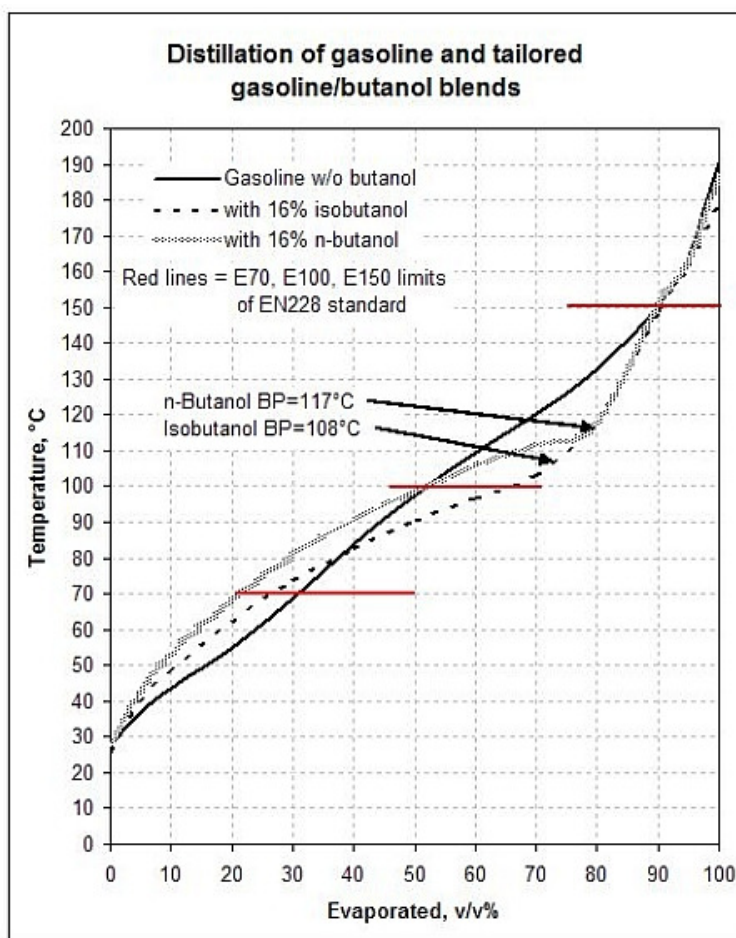
Figure 14 Example of distillation curves for gasoline and tailored gasoline/butanol blends.
EN228:2008 limits for E70, E100, and E150 limits are marked as red lines[12].

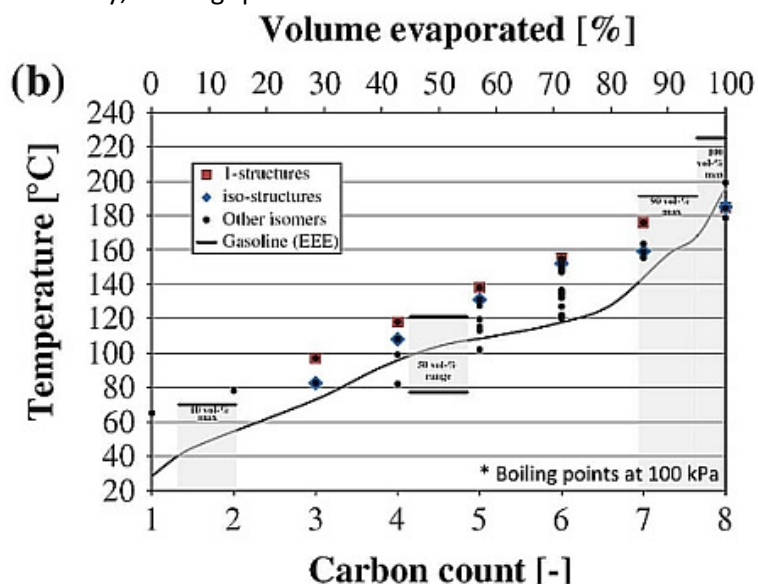Generally, boiling points of alcohols increase with increasing carbon chain length, Figure 15

Figure 15 Boiling points of alcohols and distillation curve of gasoline [11].

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Heat of vaporization

Heat of vaporization is substantially higher for ethanol than for gasoline. Higher heat of vaporization improves knock resistance and enables achieving higher engine efficiency, but also leads to problems to start up and to run the cold engine [14]. Heat of vaporization of longer chain alcohols, such as butanol isomers, is close to that of gasoline (Figure 16 and Figure 17).
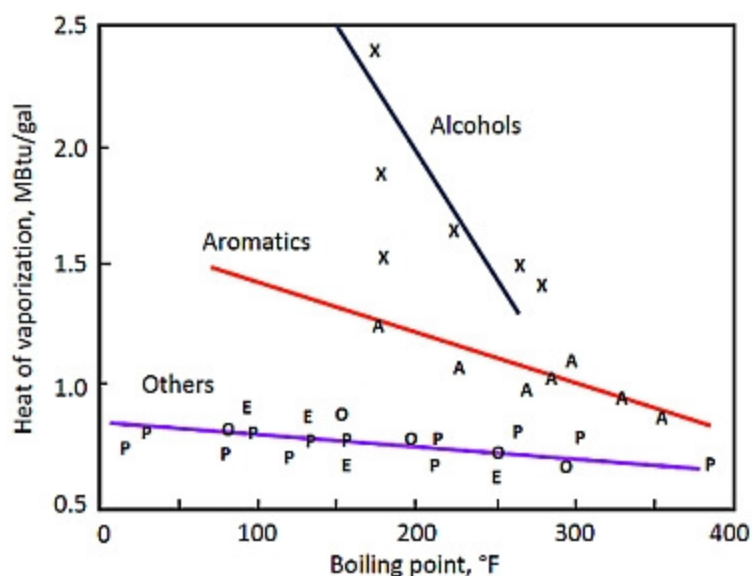

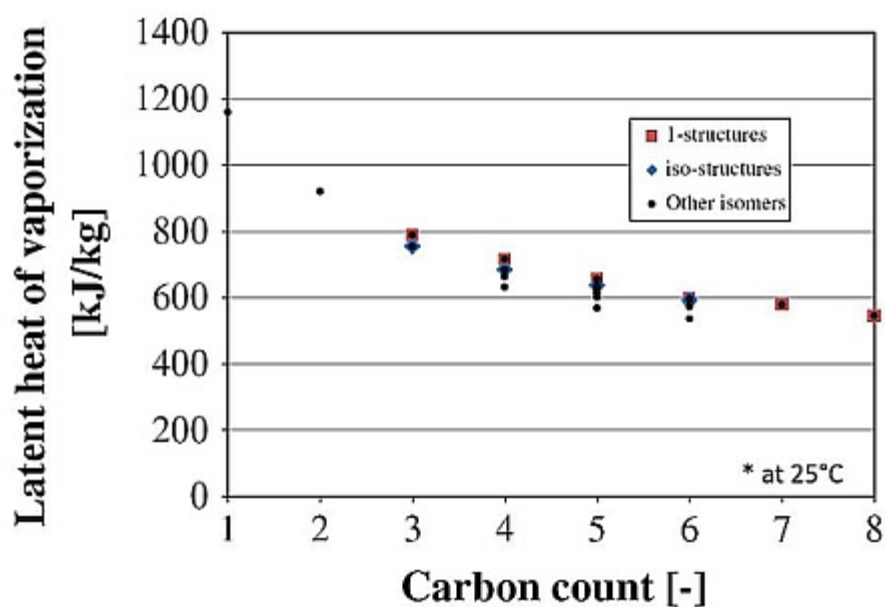Figure 16 Heat of vaporization for alcohols, aromatics, olefins (O), paraffins (P), and ethers (E) [10].

Figure 17 Latent heat of vaporization of various alcohols [11].

Flame temperatures

Flame temperatures of some alcohols are lower than those of e.g. aromatics (Figure 18). However, if alcohols lead to leaning of air to fuel ratio, combustion temperature rises [10]. Flame temperatures for butanol are close to those of gasoline.
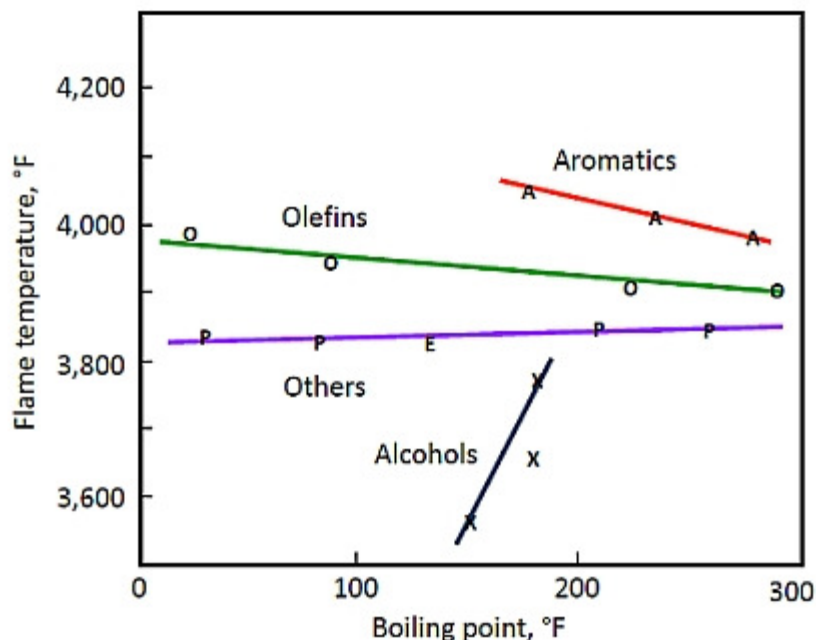

Figure 18 Theoretical flame temperatures for alcohols, aromatics, olefins, paraffins (P), and ethers (E) assuming adiabatic process and stoichiometric air to fuel ratio[10].

Energy content

Energy content of isobutanol is 33 MJ/kg (26.5 MJ/l) representing around 82% of volumetric energy content of gasoline. Densities of butanol isomers are higher than those for gasoline, which improves volumetric fuel economy to some extent. Theoretically, volumetric fuel consumption increases some 3.5% when 16 vol-% butanol is blended with non-oxygenated gasoline.

Water tolerance

Butanols are not as polar compounds as ethanol. tert-Butanol is miscible with water, but solubility of other butanol isomers are limited. Solubility of sec-butanol in water is relatively high, whereas solubilities of isobutanol and n-butanol are only around 8 wt-% at 20 °C. (BASF Technical leaflet). Isobutanol or n-butanol are not prone to migrate into water phase from gasoline in normal conditions.

Viscosity

Viscosities of butanol isomers are high when compared to gasoline. Viscosity of n-butanol is 2.7 mm2/s at 40°C, and that of isobutanol 2.3 mm2/s. These are close to viscosities of diesel fuel. For example, viscosity limits in the European diesel fuel standard (EN 590) are 2.0-4.5 mm2/s.

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Appendix 6 Methoxyl derivates

On the more unconventional ways of introducing bio-feedstock into the diesel fuel system the mixing of alcohol and other oxygen containing shorter molecules into the long chained diesel has been proposed. One direction, proposed by [1] is to introduce the cyclic oxygenated compounds benzaldehyde, phenylethanol and acetophenone, see Fig 19. These proved to mix well with the diesel and having a high density also adds more energy into the fuel. Another process of introducing oxygenated compounds into the diesel fuel is the alcohol-fueled diesel engines which have demonstrated reductions in carbon monoxide (CO), hydrocarbons (HCs) and particulate matter compared to conventional diesel engines mainly due to the extra oxygen content in the fuel, which enhancing the oxidation of soot, CO and THC [2] [3]. A comparison of properties of acetone, butanol and ethanol can be found in Fig 20. Butanol has many advantages, like high heating value, high cetane number, low vapor pressure and good miscibility comparing with diesel. Comparing to the petroleum-based butanol, ABE fermentation producing bio-butanol has received increasing attention. Acetone-butanol-ethanol (ABE) fermentation primarily involves bacterial fermentation of biomass feedstock to produce acetone, n-butanol and ethanol at volume percentages of approximately 22-33%, 62-74%, and 1-6% respectively. Also without the corrosion issues, the existing pipelines can be used for transportation. However, the high costs for ABE separation from dilute fermentation broth is the main obstacle for the industrial scale bio-butanol production.
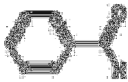
Fuel name	Diesel	Benzalde-hyde	Phenyl ethanol	Acetophe-none
Molecular structure	-			
Chemical equation	-	C_7H_6O	$C_8H_{10}O$	C_8H_8O
Density [kg/m³]	830	1050	1017	1030
Boiling point [K]	453-633	451	493	475
Molar mass [g/mol]	233	106	122	120

Figure 19 Aromatic oxygenates. Neat fuel and additive specifications [1].

Properties	Diesel[a]	Acetone[b]	Butanol[c]	Ethanol[c]
Molecular formula	$C_{12} - C_{25}$	C_3H_6O	C_4H_9OH	C_2H_5OH
Cetane number	40 min	-	25	8
Octane number	-	-	96	108
Oxygen content (wt.%)	-	27.6	21.6	34.8
Density at 15 °C (g/mL)	0.82-0.86	0.791	0.813	0.7935
Autoignition temperature (°C)	230	560	385	434
Flash point at closed cup (°C)	64	17.8	35	8
Lower heating value (MJ/kg)	42.7	29.6	33.1	26.8
Boiling point (°C)	282-338	56.1	117.7	78.4
Stoichiometric ratio	14.3	9.54	11.21	9.02
Latent heat at 25 °C (kJ/kg)	270	518	582	904
Flammability limits (vol. %)	0.6-5.6	2.6-12.8	1.4-11.2	4.3-19
Saturation pressure at 38 °C (kPa)	0.3	53.4	2.27	13.8
Viscosity at 40 °C (mm^2/s)	1.9-4.1	0.35	2.63	1.08

a Properties of diesel are from ASTM D975 and ref [13], b Properties of acetone are from ref [14][15], c Properties of ethanol and butnaol are from ref[14-16].

Figure 20 Oxygenated alkanes [2].

Further oxygeneates emerges from the ideas of introducing fuels which results from gasification of biomass. Such possible products include phenol and guaiacol as found in Figure 21
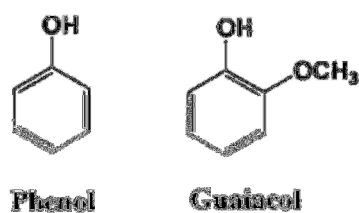

Figure 21 structures of phenol and guaiacol [4]

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Appendix 7 Exotic esters – levulinate & furoate

Ethyl levulinate can be gained from levulinic acid which is produced by acid hydrolysis of cellulose. [1] Levulinic acid, see Fig 22, is the precursor to pharmaceuticals, plasticizers, and various other additives. Potential biofuels can be prepared from levulinic acid including methyltetrahydrofuran, valerolactone, and ethyl levulinate. Levulinic esters are known as an additive for Diesel fuel to increase the oxgen content. Butyl levulinate consists of about 30% oxygen. Due to the molecular structure, particularly the small number of c-atoms and the oxygen content of an ester, butyl levulinate have a cetane number below the measurement limit [2].
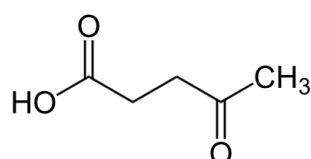

Figure 22 Levulinic acid

Another oxygenate, 5-methyl furoate ethyl ester (EF), can be mady by a chemical process from biomass and ethanol. This compound has been tested as a renewable diesel additive at concentrations up to 10 percent by volume. This ester, which is similar in composition to a known food additive, was studied for engine performance in comparison with two other oxygenated alternatives (i.e. ethanol - EtOH and ethyl levulinate - EL) and with B20 (20 percent biodiesel). The emission results indicated that a blend of the ester with diesel was comparable to the base fuel. In addition, the results also indicated that EF reduces the formation of particulate matter (PM) and carbon monoxide. Other properties of EF seem to improve the physical properties of the blended fuel such as lubricity and viscosity when compared to the base fuel, see Figure 23. [3]

FUEL CODE	TEST METHOD	ASTM D975	BASE	5% EF	10% EF	10% EL	10% EtOH	B20	B20+10% EF
Aromatics, vol %		35 max.	29.3	29.8	28.5	27.5	29.4	31.2	32.5
Olefins, vol %	D1319	NA	1.3	1.4	1.4	2.4	2.1	2.9	1.7
Saturates, vol %		NA							
Cetane Number	D613	40 min.					47.4	44.5
Cetane Index	D976	40 min.	45					47.6	39.8
Specific Gravity	D4052	NA	0.8466				0.8443		0.8764
Heat of Combustion (Gross), MJ/kg	D240	NA	45.786	44.344	43.141	43.143	45.396	44.357	41.845
Heat of Combustion (Gross), MJ/m³		NA				37.307			
Heat of Combustion (Net), MJ/kg		NA	42.624	41.653			40.611	41.617	
Heat of Combustion (Net), MJ/m³		NA							
Flash Point, °F	D93								
Viscosity @ 40 °C, cSt	D445	1.9–4.1							2.841
Lubricity, HFRR @ 60°C, μm	D6079	520 max.							
Ash, % mass	D482	0.01 max.	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Cloud Point, °C	D2500	D975 spec	-26.8	-26	-26	7	0	-8	-8
Cold Filter Plugging Point, °C	D6371	D975 spec	-27	-30	-30	-31	-30	-18	-12
Electrical Conductivity, pS/m	D2624	25 min.	129	105	544	1569	>1569	114	652
Copper Strip Corrosion	D130	No. 3 max.	1A	1A	1A	1A	1A	1A	1A
Water & Sediment, vol %	D2709	0.05 max.	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ramsbottom, wt %	D524	0.35 max.	0.07	0.08	0.08	0.08	0.08	0.04	0.02
Distillation									
IBP, °C	D86	NA	185	183	168	165	58	191	191
10%, °C		NA	214	208	206	201	81	222	213
50%, °C		NA	268	268	261	264	224	277	272
90%, °C		282 – 338	303	303	303	303	298	325	236
EP, °C		NA	331	328	330	333	325	341	339

NA-Not applicable
Saturates include all alcohols and biodiesel component in the additive; data adjusted for the additive content of each fuel.
"It is unreasonable to specify low temperature properties that will ensure satisfactory operation at all ambient conditions. The appropriate low temperature operability properties should be agreed upon between the fuel supplier and the purchaser for the intended use and expected ambient temperatures. Tenth percentile minimum air temperatures may be used to estimate the expected regional target temperatures." (ASTM D975)

Figure 23 properties of base diesel fuels and EF [3].

Other possible esters from the levulinic acid including the Butyl Levulinate (BL) and its blends with diesel was was evaluated by Christensen [4]. The pure levulinate esters, Ethyl and Butyl, was found to be very low in cetane number, see Table 21, thus making them unsuitable as pure fuels. The lower ethyl based esters was found to be prone to separate from the diesel. Mixing a small (5w%) biodiesel in the diesel-Ethyl ester made the ester stay in solution. This compared to the higher ester, butyl, which with its lower solubility in water remained in solution with diesel. Both esters were found to increase lubricity and conductivity. Ethyl levulinate contained residual levulinic acid which made acidity too high to fit within diesel specification, the Butyl esters was found to be cleaner and with lower acidity. None of the esters had any detoriating impact on emissions

Table 21 Properties of Ethyl- and Bytyl esters [4]

description	units	EL	BL
chemical formula		$C_7H_{12}O_3$	$C_9H_{16}O_3$
CAS number		539-88-8	2052-15-5
derived cetane number		<5[13]	14
melting point	deg C	< −60	< −60
boiling point[10]	deg C	206	232
flashpoint	deg C	90	110
acid value	mg of KOH/g	0.7	0.4
KF water	ppm	778	234
LHV[a]	MJ/kg	24.340	27.435
LHV	Btu/gallon	88715	95875
density	g/mL at 25 °C	1.016[19]	0.974[20]
sulfur	ppm	0.9	0.8
lubricity (wear scar)	μm	430	310
kinematic viscosity	cSt	1.50	1.99
ash	wt %	<0.001	<0.001
Ca	ppm	6	10
Mg	ppm	<1	2
Zn	ppm	4	6
solubility of water in ester	wt %	8.5	2.6
solubility of ester in water	wt %	15.2	1.3
Rancimat induction time	h	>40	>40

Table 22 Properties of Ethyl- and Bytyl esters in blends [4]

description	units	EL10	EL15/B5	BL20
oxygen	wt %	3.82	6.34	6.21
cloud point	deg C	3.3	6.8	−24.8
cloud point	deg C	3.8	8.8	−26.0
lubricity (wear scar)	μm	337	316	357
conductivity	pS/m	962	3660	2020
flashpoint	deg C	75	75	80
DCN		41.0	41.6	39.9
DCN[a]		45.0	44.5	43.4
CN				
LHV[b]	Btu/lb	17620	17112	17090
LHV	Btu/gallon	123930	121573	121450
Cu strip corrosion		1a	1a	1a
aromatics	vol %	35.4	40.4	35.2
olefins	vol %	1.6	1.7	1.7
saturates	vol %	63	57.9	63.1
sulfur	ppm	6.9	6.8	5.9
water and sediment	vol %	0.01	0.01	0.01
kinematic viscosity	cSt	2.15	2.16	2.20
ash	wt %	<0.001	<0.001	<0.001
carbon residue	wt %	0.13	0.07	0.1
distillation (T-90)	°C	298	307	295
total insolubles	mg/100 mL	0.6		0.4
Rancimat	h	36		33

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