

Investigation of naphtha-type biofuel from a novel refinery process

Author, co-author (Do NOT enter this information. It will be pulled from participant tab in MyTechZone)

Affiliation (Do NOT enter this information. It will be pulled from participant tab in MyTechZone)

Abstract

In order to reduce the carbon footprint of the Internal Combustion Engine (ICE), biofuels have been in use for a number of years. One of the problems with first-generation (1G) biofuels however is their competition with food production. In search of second-generation (2G) biofuels, that are not in competition with food agriculture, a novel biorefinery process has been developed to produce biofuel from woody biomass sources. This novel technique, part of the Belgian federal government funded Ad-Libio project, uses a catalytic process that operates at low temperature and is able to convert 2G feedstock into a stable light naphtha. The bulk of the yield consists out of hydrocarbons containing five to six carbon atoms, along with a fraction of oxygenates and aromatics. The oxygen content and the aromaticity of the hydrocarbons can be varied, both of which have a significant influence on the fuel's combustion and emission characteristics when used in Internal Combustion Engines. When used as a blend component, this novel 2G biofuel could help increase the sustainability of vehicle fuels. But, while exhaustive experimental and, although lesser in number, numerical investigations on combustion behavior have been performed for 1G biofuels, less information is available for 2G biofuels and especially this novel naphtha-like fuel. An extensive fuel compound property database and a fuel blend property calculator is readily available in literature, but their validity has not been tested for the novel 2G biofuel components.

This article provides a first screening of the usability of these light naphtha components as blend components for gasoline and diesel drop-in fuels, by means of a freely available fuel component database and fuel blend calculator, concluding with an initial assessment of achievable blends and pointing out where further work is needed.

Introduction

A society built on 100% renewable energy by 2050. That is the ambition that several European countries call for in their letter to the European Commission. Considerable efforts are required to achieve such a target, which it is not impossible to reach. Although a certain degree of electrification can be expected, a mix of technology solutions leads to the best trade-off between affordability and high CO₂ emissions reduction [1]. Advanced renewable fuels are one of the possible solutions for the transportation and aviation sector transition [2].

Amongst the different types of renewable fuels, hydrocarbon mixtures are and will remain the most efficient ones in terms of energy density. Biofuels are hydrocarbon-based renewable fuels and are typically

generated out of biomass, plants and crops that during their lifetime capture CO₂ from the atmosphere. When converted into biofuel and upon combustion in the engine, the CO₂ that once was absorbed from the atmosphere is released again. When produced in a carbon-neutral way, the biofuel's carbon cycle is hence neutral, in contrast to fossil fuels which are derived from fossilized biomass that has been stored for millions of years under the earth's surface. Biofuels can partially replace fossil fuels when blended with a fossil fuel, without affecting the operation of legacy combustion engines in use today. Fossil fuel/biofuel blends are an ideal pathway to a step-by-step replacement of fossil fuels by sustainable fuels. Currently, in Europe, B7 (a diesel fuel blend containing 7 volume% of biodiesel), E5 and E10 (gasoline with 5 and 10 volume% of bioethanol respectively) are widely in use.

However promising the use of biofuels may seem, there are many limits regarding their use in current combustion engines. Technical limits [3], ethical considerations with the first-generation biofuels[4] and the simple fact that there is not enough biomass available to fuel the world's transport needs [5]. In this context, the production of biofuels from lignocellulosic biomass is found to be an emerging trend that can help - at least partly - overcome these problems. Lignocellulosic materials are one of the most promising potential feedstocks for the production of biofuels such as bioethanol, butanol, biohydrogen, biogas (biomethane), and biooils like lignin oil. Lignocellulose can be obtained from woody crops that typically do not compete with agriculture and furthermore can be harvested on areas that are not fit for food production. Fuels derived from it are the so-called second-generation biofuels. Although care must be taken with production, one can state that the use of second-generation biofuels is considerably more ethically acceptable than first-generation biofuels [6].

The Ad-Libio project aims to develop novel advanced 2G biofuels to support the decarbonization of the transportation sector. The biorefinery process designed by researchers at KU Leuven [7] generates biofuels that can blend with fossil diesel or fossil gasoline to obtain so-called drop-in fuels, which cannot be distinguished from current fuels by the engines in use today.

The end products of the new process differ considerably from that of the more common biofuel products like biodiesel (FAME) or ethanol. It consists mainly of naphtha-type molecules and oxygenates. Being different from the products that are typically used in fossil fuel/biofuel blends, their usability in transportation fuel needs to be examined. In this paper, we will investigate the potential of this new biofuel as blend components for drop-in fuels for diesel and gasoline engines. We'll examine the impact on the most important fuel properties for SI engines and CI engines by means of a readily available fuel blend

property calculator [8] and a fuel compound property database [9]. The blend properties will be compared against the European Norms for gasoline and diesel fuel (respectively EN228 and EN590) to investigate whether blends with the new 2G biofuel components would be applicable in the short term as a replacement for the commonly used 1G biofuels.

We will first take a look at the origin of the 2G biofuel itself, after which we will discuss the most important fuel parameters for SI and CI engines and relate them to the current European fuel norms. We continue with calculations of blended SI and CI fuel properties to be able to estimate the potential of the naphtha biofuel and to conclude on further work to be done.

Lignocellulosic biofuel explained

The production of biomass-based hydrocarbon fuels depends on many factors, such as biomass feedstock, the desired fuel type and the chosen production process itself. Whichever process is chosen, to make a biofuel truly renewable, the production must rely on renewable energy (e.g. green electricity or energy from renewable fuels). Renewable carbon can be found in lignocellulose, a polymeric composite in biomass, which provides rigidity to the plant and protects it against microorganisms. Second generation lignocellulosic biomass, derived from wood crops and agricultural residue whose consumption does not interfere with human needs, are abundantly available and cheap, making them interesting feedstocks for emerging biorefinery applications. The structural and chemical features of lignocellulose vary strongly between different feedstocks but in general, lignocellulosic biomass can be divided into hardwood, softwood and grasses, as shown in Table 1 [10]

Table 1. Example of lignocellulosic biomass classification, based on chemical composition.

% dry weight	Hardwoods		Softwoods		Grasses	
	Birch	Willow	Pine	Spruce	Corn Stover	Rice straw
Cellulose	38.2	43.0	46.4	43.4	35.6	34.2
Hemicellulose	19.7	29.3	22.9	18.0	22.1	24.5
Lignin	22.8	24.2	29.4	28.1	12.3	11.9
NSC ¹	19.3	3.5	1.3	10.5	30.0	29.4

¹NSC includes non-structural compounds such as fats, oils, proteins, terpenes and others in low concentrations.

Each individual component of the lignocellulosic matrix has its intrinsic characteristics. While the first lignocellulosic building block, cellulose, exclusively exists of regularly ordered C6 sugars (e.g. glucose), the second building block, hemicellulose, contains diversely arranged C6 (e.g. mannose, galactose) and C5 sugars (e.g. xylose, arabinose). Because of their relatively simple carbon skeleton, which can be cleaved into the desired hydrocarbon mixtures, cellulose and hemicellulose seem the most interesting ones to create hydrocarbon-based biofuels. By contrast, the third lignocellulosic building block, lignin, looks very different due to its irregularly incorporated C9-C11 phenols. Notwithstanding the fact that it is not used in the Ad-Libio process, this lignin fraction could also serve as a biofuel precursor, creating different hydrocarbon mixtures with other fuel properties. As a consequence of their weak or unsaturated atom bonds, these biopolymers have a high degree of affinity to bind with hydrogen atoms. Hydrogen can therefore be used as a component to increase the

energy density of the lignin-based polymers. Also, the Ad-Libio process uses hydrogen affinity to add green hydrogen (hydrogen from renewable sources like wind or solar energy) to the cellulosic and lignocellulosic polymers, which can therefore be considered as effective hydrogen energy acceptors. This makes the Ad-Libio process a hybrid process, where green carbon is combined with green hydrogen to form a combustible hydrocarbon mix.

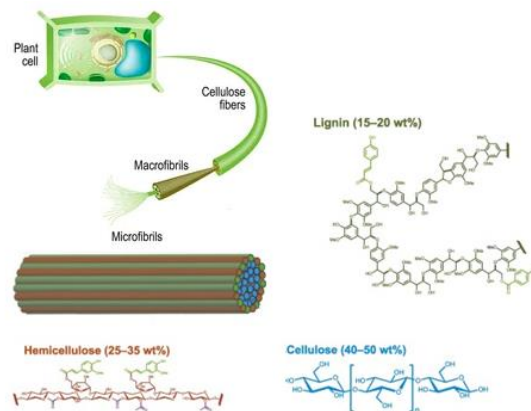


Figure 1. The different components of the lignocellulosic matrix

Before individual lignocellulosic components (i.e. cellulose, hemicellulose, lignin) can act as a biofuel precursor, raw biomass needs to be disassembled. For this purpose, the wood is mechanically treated (e.g. debarked, cleaved, milled) to enable further processing. Next, the obtained wood particles undergo basic extraction of the non-structural compounds such as fats, oils, proteins and terpenes, which can be used for other bio-based applications. In a first step of the actual biomass fractionation, (step 1, Figure 2), lignin is extracted from the lignocellulosic network in the presence of an alcohol solvent and subsequently stabilized by catalytically depolymerizing it in stable fragments. Due to the mild reaction conditions (i.e. temperature and hydrogen pressure), cellulose and a large part of hemicellulose stay untouched throughout this refinery process. So besides the lignin oil a solid pulp is retained, which predominantly consists of C6 and C5 sugars. This fibrous sugar pulp is the ideal source for implementation of energy-rich hydrogen molecules, yielding a hydrocarbon mixture in the naphtha-range (C5-C6 molecules)[7]

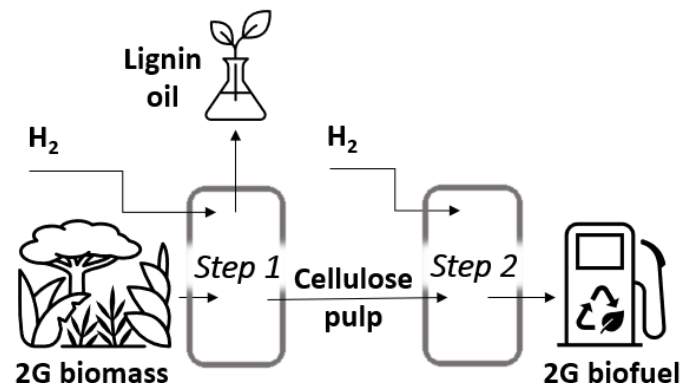


Figure 2. Overview of the novel bio naphtha process

Bioethanol production from 1G feedstock is a well-developed and well-established sugar upgrading method. However, Bioethanol

production from 2G feedstock involves enzymatic saccharification followed by sugar fermentation through yeast cells. One disadvantage of this 2G bioethanol process can be found in the fact that not every sugar type is transformed with the same efficiency due to type affinity differences with yeast cells. But more importantly one third of the carbon feedstock is released as carbon dioxide during ethanol formation, which not only is a greenhouse gas but it also means that the available carbon is used inefficiently. Also, scaleup hurdles such as huge cost of the enzyme cocktails for saccharification and poor growth of fermenting microorganisms in industrial environments may hinder the breakthrough of this saccharification process from 2G feedstock. Compared to 2G bioethanol production through fermentation, the bio naphtha production process has some advantages. This process is used in the second part of the biorefinery process (*step 2, Figure 2*). A selective conversion, only possible in a biphasic solvent system, takes place. Each liquid phase contains its own catalyst with its own specific function. Reactions take place under relatively low temperature (250°C) and relatively low hydrogen pressure (50 bar), making it a mild and sustainable approach compared to more energy-intensive processes like gasification (800-900 °C), pyrolysis (300-500 °C) or liquefaction (200-250 °C but at elevated pressures of 100-250 bar). In the aqueous compartment, the (hemi)cellulosic pulp is broken up into its monomeric sugars (i.e. glucose, mannose, galactose, xylose, arabinose). Subsequently, these sugars are dehydrated to (hydroxymethyl)furfural intermediates, losing part of the oxygen in the form of water. As a result of the intermediates' changing solubilities regarding the different solvents, the next reaction steps occur in the organic compartment. In short, these transformations lead to a further oxygen removal, by adding renewable energy to the molecules in the form of hydrogen. As an end result, this cascade gives rise to hydrocarbons containing five to six carbon atoms in their skeleton. The most prevalent components are hexane, pentane, methyl cyclopentane, 2-methylpentane, cyclopentane, 2,5-dimethyltetrahydrofuran, all of which could act as fuel components for internal combustion engines. The last four molecules are oxygenates. It should be noted that the amount of oxygen in the outcome of the process can be regulated by controlling the amount of hydrogen. The more hydrogen used in the process, the lower the amount of oxygenates in the resulting naphtha biofuel and the higher the volumetric energy content.

Table 2. Typical outcome of the Ad-Libio process

Biofuel component	Volume %
n-hexane	70
n-pentane	13
methyl cyclopentane	9
2-methylpentane	1
cyclopentane	1
3-methylpentane, methyl/ethyl/propyl cyclohexane, butane, methylpropane	5
tetrahydropyran, dimethyl tetrahydrofuran, methyl tetrahydrofuran	1

To avoid waste production, each output stream needs to be purified for further use or recycling. First, the gaseous phase, mainly comprising residual hydrogen, butane, propane and methane, is removed from the liquid reaction mixture. Second, the aqueous and organic layer, together forming the liquid phase, are separated from each other. The aqueous compartment can be recycled without additional treatment, since it remains untouched during reaction. Unreacted intermediates which are possibly left behind, will be converted in a subsequent run. The organic compartment on the other hand, is further treated by separating the naphtha-type biofuel from the less volatile solvent. This organic solvent can be reused, producing no direct waste streams overall. It is worthwhile mentioning that the Ad-Libio project incorporates a technical-economic analysis, which includes purity requirements for the (green) hydrogen, along with an overall cost analysis of the fuel's production process.

Now the typical biofuel process outcome is known, we can look into the fuel properties and their compatibility with applicable European fuel norms in use today.

Fuel properties versus European fuel norms

Many research has been done on fuel properties that increase the efficiency of Spark-Ignition (SI) [11] and Compression-Ignition (CI) [3] engines. The following fuel properties are only a few of many, but in the context of this work they can be considered amongst the most important ones. Depending on whether the engine is spark-ignited or compression-ignited, the desired fuel properties differ. For SI engines, volatility and knock resistance are two of the most important parameters affecting engine performance. Low fuel volatility can hinder air-fuel mixture formation and high volatility can prevent fuel flow by creating vapor bubbles in the fuel lines with increasing temperature. Knock resistance, on the other hand, prevents the fuel from igniting inadvertently in the end-gas region. Knock should be avoided to prevent non-optimal engine performance or engine damage. As a measure for knock resistance, the fuel's Octane Number (ON) is used. Heavily simplified, the octane number is inversely proportional to the chain length of the fuel molecules and directly proportional to the number of branched side chain components. Also, the presence of cyclic molecules, alcohols, and aromatics tend to increase the fuel's octane number.

For CI engines, important fuel properties are viscosity, lubricity, and ignition tendency. CI fuels with lower viscosity require less pumping work. Low fuel viscosity reduces the fuel's surface tension, resulting

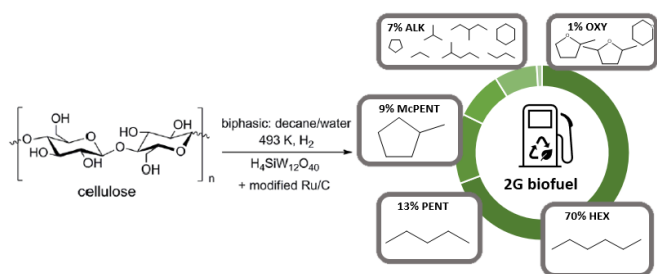


Figure 3. Process outcome, simplified

A typical biofuel composition of the naphtha process outcome can be found in Table 2.

in a smaller fuel spray droplet diameter leading to better fuel combustion. But also a good tendency for the fuel to self-ignite is important for CI engines. The fuel's cetane number is used as a measure of its ignition ability. High cetane numbers for CI fuels lead to low Ignition Delay (ID). Lower ignition delay brings benefits, like increased fuel economy, fewer emissions or increased power output. Finally, lubricity, which can be described as a substance's anti-wear property is equally important, since the fuel takes part in the fuel injection equipment lubrication process.

In order to harmonize gasoline and diesel fuel properties, fuel norms in Europe (and elsewhere) have been subject to a legal framework. The first set of CEN standards in 1993 for automotive fuels were voluntary, but were observed by all fuel suppliers in Europe. Two standards covered automotive fuel quality for diesel and gasoline: EN 590 for diesel, EN 228 for gasoline. Mandatory environmental regulations for several fuel properties were first introduced in 1998. The current legislation regarding gasoline fuels is to be found in the European Norms EN:228:2012+A1:2017 and for diesel fuels in EN:590:2013+A1:2017.

In Tables 3 and 4, the most relevant required EN properties are listed. It can be seen that the properties are different for gasoline (SI) engines compared to their diesel (CI) counterparts.

Table 3. extract of EN:228:2012+A1:2017 for gasoline fuel

Gasoline E10 required EN properties	
RON (min)	95
MON (min)	85
Max volume% olefins	18
Max volume% aromatics	35
max mass% oxygen content	2.7
Max volume% methanol	3
Max volume% ethanol	5
Max volume% iso-propyl alcohol	until 2.7 oxygen mass% is reached
Max volume% ter-butyl alcohol	until 2.7 oxygen mass% is reached
ethers (5 or more C-atoms)	until 2.7 oxygen mass% is reached
Other oxygen containing molecules	until 2.7 oxygen mass% is reached
Vapour pressure (kPa)	45-60 or 70-100, depending on class

Table 4: extract of EN:590:2013+A1:2017 for diesel fuel

Diesel B7	
Cetane number (min)	51
mass density at 15°C	820 - 845 kg/m ³
max mass% polycyclic aromatic hydrocarbons	8
flash point	> 55°C
Lubricity (WSD) at 60°C	max 460 µm

Distillation vol% at 250°C	<65
Distillation vol% at 350°C	>85
95% distillation point	max 360°C

Thanks to a Fuel Property Database (vom Lehn et al.)[9], the relevant properties of each naphtha-type fuel component can be looked up. Vom Lehn's database contains more than 600 potential SI engine fuel components. It contains the characteristic fuel properties such as those indicating knock resistance and potential efficiency benefits. The database is available on Aachen University's website[12]

The tool is based on Microsoft Excel and is easy to use. The fuel compound for which the properties are requested can be entered in a search field (see Figure 4), after which the data becomes available to the user.

Fuel Database Search Engine

Fuel property database corresponding to: A property database of fuel compounds with emphasis on spark-ignition engine applications, Preprint submitted to Applications in Energy and Combustion Science (2020).

This search engine only provides a quick overview of fuel property data. Detailed information on the fuels, their property values as well as metadata, explanations, and references are provided in the other worksheets of this document.

Name of Compound (optional):

CAS number (optional):

Formula: <input type="text" value="C6H14"/>	Fuel class: <input type="text" value="Linear alkanes"/>
Molecular Weight: <input type="text" value="86.17536"/> g/mol	SMILES code: <input type="text" value="CCCCCC"/>
Boiling Point: <input type="text" value="69"/> °C	Melting Point: <input type="text" value="-95.3"/> °C
Heat of Vaporization: <input type="text" value="365.5"/> kJ/kg	Vapor Pressure: <input type="text" value="20.4"/> kPa
Lower Heating Value: <input type="text" value="44.5"/> MJ/kg	Density: <input type="text" value="654.7"/> kg/m ³
Kinematic viscosity: <input type="text" value="0.498"/> mm ² /s	Surface Tension (prediction): <input type="text" value="20.3 ± 3"/> mN/m
Solubility: <input type="text" value="0.0095"/> g/L	Oxygen content: <input type="text" value="0"/> wt%
H/C ratio: <input type="text" value="2.33"/>	
RON: <input type="text" value="24.8"/>	MON: <input type="text" value="26"/>
Blending RON: <input type="text" value="19"/>	Blending MON: <input type="text" value="22"/>
RON (ANN prediction): <input type="text" value="27.2"/>	MON (ANN prediction): <input type="text" value="27.8"/>
OS (ANN prediction): <input type="text" value="0.3"/>	

Figure 4: fuel property database lookup result for n-hexane. The database contains more than 600 fuel components

Several naphtha fuel components from the novel process were looked up from the database and are listed against the EN228 (gasoline) norm in table 5. It is clear that the renewable light naphtha-type fuel is non-compliant with the features listed in the EN228 norm and that the fuel by itself cannot be used as-is.

Table 5: Properties of some of the naphtha process products, compared to EN228 requirements for gasoline fuel. Next to the RON and MON indication, components that are limited in quantity (expressed in maximum vol%) by the fuel norm are indicated as ‘not ok’ (nok) by which is meant that they must be limited in quantity to comply as a fuel blend component.

	RON (min)	MON (min)	olefins (alkenes)?	aromatics?	oxygen content?	ethers?	Other oxygen containing molecules
Gasoline E10	95	85	max 18 vol%	max 35 vol%	max 2.7 mass%	until max 2.7 mass% oxygen	until max 2.7 mass% oxygen
n-hexane	24.8	26	ok	ok	ok	ok	ok
n-pentane	61.7	61.9	ok	ok	ok	ok	ok
Methyl cyclopentane	91.3	80	ok	ok	ok	ok	ok
cyclopentane	101.3	85	ok	ok	ok	ok	ok
2-methylpentane	73.4	73.5	ok	ok	ok	ok	ok
2,5-dimethylfuran	101.3	88.1	nok	ok	nok	nok	ok

Looking into the requirements for diesel fuel, we turn back to the fuel property database. Even if it was conceived as a spark ignition fuel database, it is still suitable for compression ignition fuels. For most fuels, the derived cetane number is available. Flash point and lubricity are parameters that are not available for lookup in the database. The flash point FP however, according to Prugh et al. [13], can be estimated by use of Eq. 1 from the boiling point BP, both expressed in degrees Celsius.

$$FP = 0.683BP - 66 \quad (1)$$

Viscosity properties of diesel fuel are well defined in the EN590 norm and vom Lehn’s database has the data available for most naphtha components. Lubricity is an important parameter for diesel engines. Diesel fuel pumps used in common-rail systems of modern passenger cars and heavy duty applications rely on fuel lubrication, so a minimum lubricity of diesel fuels needs to be guaranteed. While viscosity data is available in vom Lehn’s database, lubricity data is not. However, lubricity information on some components is available through Weinebeck et al. [13] For most components however, lubricity data is not available and should be predicted. Lubricity and viscosity are two different but related things, however, nothing was found in literature to provide insight in the relationship between fuel viscosity and lubricity of naphtha fuel components.

The fuel property data that was available at this point was consolidated and can be found in Table 6.

Table 6: Properties of some of the naphtha process products, compared to EN590 requirements for diesel fuel. Next to the cetane indication, components that are limited in quantity (expressed in maximum mass%) by the fuel norm are indicated as ‘not ok’ (nok) by which is meant that they must be limited in quantity to comply as a fuel blend component.

	Cetane number	Viscosity (mm ² /s)	Max density	Max mass% aromatic HC	Flash point	Lubricity	Dist vol% at 250°C	Dist vol% at 350°C
Diesel B7	51	Between 1,50-4,00	820-845 /m ³	8	>55°C	Max 460 µm	<65	>85
n-hexane	44.8	0.498	654.7	ok	-18°C	n/a	Boiling pt 69°C	
n-pentane	30	0.36	685.9	ok	-41°C	n/a	B. pt. 35.2°C	
Methyl cyclopentane	17.2	0.68	743.3	ok	-17°C	n/a	B. pt. 71.8°C	
Cyclopentane	6.1	0.56	740.5	ok	-32°C	n/a	B. pt. 49.5°C	
2-methylpentane	34	n/a	73.5	ok	-24°C	n/a	B. pt. 60.6°C	
2,5-dimethylfuran	10.9	0.57	88.1	nok	-3°C	855	B. pt. 93°C	

Also here we can conclude that the naphtha fuel components do not comply with the EN590 norms for diesel fuel.

Now that most fuel properties of the light naphtha type are known, we can look further into their behavior when blended with gasoline or diesel.

Blend property calculations

Previous research with SI and HCCI engines [14-16] has revealed interesting potential for using naphtha-type fuel components in low temperature combustion concepts, but these fuels cannot be considered as EN590 or EN228-compliant. Considering an EN228-compliant E10 gasoline fuel where octane number, along with the maximum amount of oxygen and aromatics content is given, the goal is to create an EN228-compliant fuel with naphtha-type blending components instead of bioethanol.

Typically, BOB blends are used to create gasoline blends with fossil and sustainable components. BOB stands for “Before Oxygenate Blending”, an unfinished gasoline blend that only lacks the addition of the predetermined volume of oxygenates (typically ethanol) to be a

finished (e.g. E10) gasoline. BOB blends could be used to formulate EN228-compliant blends with naphtha-fuel components.

In order to predict the properties of gasoline, blended with naphtha components, a fuel blend property calculator[8] is used. The project undertaken by the calculator's author Vinke resulted in a tool for computation of fuel blending characteristics. These tools exist in the industry but have large budgets for development behind them and are undisclosed to the public. In addition to this, these tools are highly complex with specific software packages associated to them. The tool created by Vinke acts as a publicly available calculator using Microsoft Excel. Excel was chosen due to its ease of use, easy database management and mass accessibility. By implementing a dynamic database and an automatically updating script within the dataset, it is possible for the user to select new database entries without any modification to the script or worksheet. The tool is capable of computing fuel mixture characteristics for any variation of fuel blends. The layout of the tool includes one worksheet for the database, one for the calculations and one for input and outputs of the desired values. In the database worksheet of the calculator, blend components are entered with their respective properties (mostly available in vom Lehn's database). Requested input data is name, type, density, LHV, molar mass, CxHyOz, stoichiometric laminar flame speed, RON, MON, Reid Vapor Pressure. The user can select up to six blend components using a drop-down menu and input the volume fraction of each blend component. The drop-down menu works in conjunction with the database worksheet and automatically recognizes any fuels that previously have been added to the calculator's database. A validation of the tool was done by developer Vinke, against blend values from literature. Next to dual blends used for validation, more complex ternary ones were taken from the paper by Turner et al.[17]. The ternary blends investigated in this paper consisted of gasoline 29.5%, ethanol 42.5%, methanol 28%; and gasoline 37%, ethanol 21%, methanol 42%. The resulting deviations of the calculated fuel properties relative to the measured ones, are shown in Table 7.

Table 7: Validation of the fuel property calculator with Gasoline-Ethanol-Methanol blends and overview of the data generated by the calculator

	Property	Measured	Fuel properties calculator	% Difference
Blend 1	RON	108.70	106.78	1.78
	MON	90.30	88.68	1.81
	LHV (MJ/L)	22.70	22.65	0.22
	Stoichiometric AFR	9.69	9.84	1.54
	Volumetric CO2 (kg/l)	1.62	1.62	0.00
Blend 2	RON	108.50	106.57	1.79
	MON	90.30	88.32	2.22
	LHV (MJ/L)	22.71	22.66	0.22
	Stoichiometric AFR	9.71	9.89	1.84
	Volumetric CO2 (kg/l)	1.62	1.62	0.00

The comparison between the results from the study of Turner et al. and the calculated fuel properties with ternary blends showed minimal discrepancies. The maximum error is 2.22%, all other errors are below 2% and some are close to or at 0%. The validation for the blending calculator was successful for the chosen components and the blending logic works for multi-component blends.

Naphtha blend property calculations for SI fuels

Should the blend property calculator show the same accuracy for other fuel types than gasoline, methanol and ethanol, a prediction could be made for fuel blends based on naphtha-type fuels. Table 2 gives an overview of the typical Ad-Libio fuel components and their respective quantities. Being limited to a maximum input number of six, the blend calculator does not have enough blend component input capability for a direct calculation of a blend with all aforementioned components. Next to that, the minimum required volumetric percentage input is limited to 1 vol% per component. As a workaround to the problem, the blend calculation of the naphtha-based fuel blend will be executed in three steps.

First, the blend calculation of the three oxygenate components is made. An even mixture of tetrahydropyran, 2,5-dimethyltetrahydrofuran and 2-methyltetrahydrofuran results in a blend with a RON of 75,4 and a MON of 61,29 according to the calculator. However, on the blend calculator's result sheet in Figure 5 we immediately see that an important calculation result is lacking. Vapor Pressure is not available for any of the aforementioned components in vom Lehn's database. Therefore, property calculations for gasoline blends will be limited to RON/MON calculations only.

Blend Properties Calculation					
Components		1	2	3	
User Entry		Tetrahydropyran	2,5-dimethyltetra	2-methyltetrahyd	
Volume Fraction		0,34	0,33	0,33	
Mass Fraction		0,35	0,32	0,33	
Mole Fraction		0,37	0,29	0,35	
Energy Fraction		0,35	0,33	0,33	
Resulting:					
Density (kg/m ³)	LHV (MJ/kg, (MJ/l) below)	Molar mass (kg/kMol)	Stoichiometric AFR	Volumetric energy density (MJ/l)	
853,52	33,68 28,75	90,17	11,33	28,75	
Oxygen Content by mass in %	RVP (kPa)	HoV (kJ/kg)	Stoichiometric laminar flame speed (cm/s)	Stoichiometric laminar flame speed (cm/s)	
17,77	0,00	268,43	Modified Le Chatelier Method	Energy Fraction method	

Figure 5. Partial screenshot of the calculator's outcome for a blend of tetrahydropyran, 2,5-dimethyltetrahydrofuran and 2-methyltetrahydrofuran, calculated at 34,33 and 33 vol% respectively. RVP returns zero due to lack of information in the fuel database.

Assuming the blend RON/MON calculation to be correct, we now have an oxygenates blend component, named "Oxygenates" which is then input in the calculator's database as one single component.

The same calculation was made with the 5% volume fraction of the non-oxygenates: 3-methylpentane, methyl- and ethyl cyclohexane, butane and methylpropane. Since propyl cyclohexane was not

available in vom Lehn's database, it was not included in the calculations. The calculation resulted in a blend with a RON of 58,39 and a MON of 55,84 and was entered in the calculator's database as one component named "Non-Oxygenates".

With these intermediate results taken into account and entered into the calculator, the properties of the typical naphtha fuel can be calculated. In volume % we calculate a blend of 70% n-hexane, 13% n-pentane, 9% methyl cyclopentane, 5% "non-oxygenates" and 1% "oxygenates". The 1% 2-methylpentane and 1% cyclopentane are not taken into the calculation at this time due to the input restriction of six components. According to the calculator, the naphtha-fuel blend results in a fuel with a RON of 41,46 and a MON of 40,32. It is put into the calculator's database as "naphtha fuel". A final calculation was made with the remaining 1 vol% 2-methylpentane and 1 vol% cyclopentane, resulting in a final calculated RON of 42,55 and a MON of 41,22

Table 8: Calculation of the octane number of the naphtha fuel blend, apart from 2-methylpentane and cyclopentane

	RON	MON	vol ratio
n-hexane	24.8	26.0	0.7
n-pentane	61.7	61.9	0.13
methyl cyclopentane	91.3	80	0.09
3-methylpentane, methyl- and ethyl cyclohexane, butane, methylpropane blend: "non-oxygenates"	58.39	55.84	0.05
tetrahydropyran, 2,5-dimethyltetrahydrofuran, 2-methyltetrahydrofuran blend: "oxygenates"	75.4	61.29	0.01
Blended naphtha fuel calculation	42.55	41.22	

These RON and MON values will now be evaluated further in order to estimate the requirements of the gasoline BOB (base) fuel.

The search for EN228-compliance

Considering RON/MON calculations only, the calculator is now used in an attempt to make an EN-228 compliant fuel blend. A maximum of 2.7 mass% of oxygenates is taken into consideration (Table 3) as a limiting parameter. In this exercise, gasoline is defined as an average C₈H₁₄ molecule, with a RON of 95 and a MON of 85. The volumetric content of the naphtha fuel is increased until the maximum oxygenate mass% of 2.7, the EN228 limit, is reached. The conclusion is that a maximum volume percentage of 16 vol% can be obtained with naphtha fuel blends. With a RON 95 BOB fuel, this would however result in a fuel blend with a RON of 84,60 which is not EN228-compliant. Reverse calculation would require a BOB fuel with a RON of 108 in order for the blend to be EN228-compliant (RON 95) and with a maximum of 2.7 mass% of oxygen content. The calculator proves to be a good tool for reverse calculations to calculate base fuels. However, its accuracy needs to be verified for the naphtha components used in the calculation. Heat of vaporization is available in both the database and the calculator but was not considered in the calculation since it is a property that is not listed in the EN228-norm.

For now, nothing can be concluded regarding vapor pressure compliance, nor can conclusions be made for other important fuel properties like laminar flame speed data since both properties are available in the calculator but are not available in vom Lehn's database. Propyl cyclohexane is not present in the database altogether.

Diesel blend property calculations and EN590-compliance

Where the fuel property calculator shows good usability with regards to SI fuel blends, it does less so for diesel fuel blends. Derived cetane numbers are available in vom Lehn's database for most components, as seen in Table 6. The cetane number of blends can be predicted, the mixing law for blended cetane number being a linear combination of the cetane numbers, based on the volumetric fraction of the components[18]. And even if there is evidence that the linear assumption is not always correct[19], we will assume the linear approach to be satisfactory for now. Based on linear blend behavior for cetane numbers, Table 9 provides the calculated cetane number of the typical light naphtha blend components. The calculator does not provide cetane number calculations, so this was done manually.

Table 9: Calculation of the derived cetane number of the naphtha fuel blend

	derived cetane number	vol ratio	cetane contribution
n-hexane	44.8	0.7	31.4
n-pentane	30.0	0.13	3.9
methyl cyclopentane	17.2	0.09	1.5
2-methylpentane	34.0	0.01	0.3
cyclopentane	6.1	0.01	0.1
butane/methyl- ethyl cyclohexane	26.9	0.05	1.3
2,5-dimethylfuran	10.9	0.01	0.1
blended naphtha fuel	derived cetane number		38.7

For calculation of the derived cetane number of the blended naphtha fuel, 3-methylpentane, propyl cyclohexane, and methylpropane proved to be in the database without derived cetane number data. The derived cetane number of butane, methyl- and ethyl cyclohexane was available, so an average number for those components was used instead.

To calculate the cetane requirement for a diesel BOB, looking at Table 6, we find the only possible limitation, next to the minimum cetane number, being the maximum of 8 mass% of aromatic hydrocarbons. Since the volumetric content of oxygenates in the naphtha fuel is limited to 1vol%, we can conclude that the 8% mass limit will never be reached and that the cetane number of the blend will be the limiting factor.

Diesel/naphtha blends that result in a fuel with cetane number of 51 are listed in Table 10.

Table 10: volume fractions of naphtha fuel to result in a cetane number of 51 for the blend, as a function of the base fuel's cetane number

Base fuel cetane number	vol% naphtha allowed for cetane number of 51
70	60%
60	42%
55	25%

Looking at cetane number alone, and given a base fuel cetane number that is high enough, important fractions of diesel blends could become sustainable when blended with the naphtha fuel components from the Ad-Libio process. However, no conclusions can be made as of yet for other important diesel fuel parameters. Flash point data can be estimated from a fuel's boiling point, but flash point calculations for blended fuels were not found in literature. Lubricity is a parameter that suffers from lack of data for most naphtha fuel components used in this study. Next to that, literature around lubricity behavior of blends with the light naphtha type was not found. However, blends of methanol, ethanol, propanol, butanol, and pentanol with diesel fuel have been analyzed[20]. It is shown that the lubricity of blends decreases with alcohol content, but this effect is partially compensated by the alcohol volatility. This relationship should be verified with naphtha fuel components. Also, viscosity predictions are available for diesel/biodiesel blends and equations have been derived that can predict blend viscosity using molar and volume fractions and temperature [20, 21]. Some equations predict the viscosity of blends using the fuel's molar and volume fraction and temperature. Observations made evident that for the prediction of the viscosity of petroleum mixtures, a simple linear law was never exactly obeyed and the greater the difference in the viscosities of components, the greater the error. Kanaveli et al. [21] concluded that the majority of mixing rules predicted viscosities of blends with oxygenates with poor accuracy. However, a more accurate estimation was developed, based on Grunberg and Nissan's model, resulting in Eq 2.

$$\ln(v_{\text{blend}}) = x_1 \ln(v_1) + x_2 \ln(v_2) + x_1 x_2 g \quad (2)$$

Where x is the molar fraction of the component and g is a parameter, defined as:

$$g = 0.053 \ln(\ln(v_1/v_2)) + 0.004 \quad (3)$$

It remains to be verified if the same rules apply for naphtha fuel components, and especially if more than two components are used in the blend.

Summary/Conclusions

In search of second-generation biofuels, a promising novel process has been developed. It is a carbon and energy-efficient process, based on woody biomass and hydrogen, with an outcome that differs from the biofuels that are in use today. The processes' end products are mainly of the naphtha type, light hydrocarbons, with properties that lean towards gasoline but could be useful with diesel blends as well.

The naphtha-type biofuel components as such do not comply with the European norms for gasoline or diesel fuel.

A publicly accessible fuel database and an Excel-based fuel property calculator have been chosen to perform some preliminary calculations to estimate the usability of naphtha-type biofuels to create drop-in fuel blends, that are compliant to the EN228 and EN590 norms for gasoline and diesel fuel respectively.

With regards to RON compliance with the EN228 norm, naphtha-type fuels could be used in SI gasoline blends up to 16 vol% , if the BOB base fuel would have an octane rating of 108. However, other blended fuel properties could not be calculated, mainly due to missing information in the fuel property database. In the case of propyl cyclohexane, no data was found altogether. Furthermore, the realism of obtaining a BOB base fuel with an octane rating of 108 without the use of oxygenates, will need further investigation.

Also for CI diesel blends, naphtha-type fuels could be used as a blend component and be compliant with the EN590 for cetane number. Volume ratios of 25% and up are possible, if the base fuel has a cetane number of 55 or more. But other important properties like flash point, viscosity and fuel lubricity cannot be calculated due to lack of information in literature for the naphtha components of the Ad-Libio process. Information on other fuel components is available however, so further research should be performed to verify if the existing relationships for those components apply for the naphtha components.

The fuel property calculator should be verified for correctness with the naphtha-type fuels used in this study before any further firm conclusions can be made. Next to the calculator verification, expansion of the calculator's number on input fuels is necessary, as well as the possibility to use volumetric percentages below 1 vol%. It would allow on-the-spot calculations for optimization of naphtha fuel composition. A good improvement for the calculator would be to add cetane number calculations for CI fuels. Next to that, calculations for lubricity, flash point and viscosity would be necessary in order to predict CI fuel behavior.

The data from vom Lehn et al.'s fuel property database proves to be an efficient tool, especially in combination with the fuel property calculator. Some properties in the database are missing, however. Vapor pressure information was missing for some components. Lubricity information is simply not available, which is understandable since the database is more oriented toward SI engine fuel. The challenge of insufficient data will be solved by obtaining it through other sources, at least for the Ad-Libio components, so proper calculations can be made. To make the fuel calculator more versatile, the implementation of other fuel parameter calculations will be considered. Experiments will be performed to verify the calculator's outcome.

As for the Ad-Libio process itself, the composition of the process outcome can be varied, especially with regards to the oxygen content. Further research is necessary to explore the boundaries of the naphtha fuel composition to see which process outcome would be optimal for SI engine fuel blends and which outcome would be best for CI fuel blends. Also, it was noted that the lignin is not a part of the reaction process. Lignin oil is removed from the process outcome. Investigation on the usability of the lignin molecules in the Ad-Libio process is necessary to see whether they could be useful to enhance the properties of the naphtha blend with regards to EN228 or EN590-compliance.

References

1. Bureau, B.F.P., *Vooruitzichten van de transportvraag in België tegen 2040*. 2019.
2. Limpens, G., H. Jeanmart, and F. Maréchal, *Belgian Energy Transition: What Are the Options?* Energies, 2020. **13**(1): p. 261.
3. Hoekman, S.K., et al., *Review of biodiesel composition, properties, and specifications*. Renewable and sustainable energy reviews, 2012. **16**(1): p. 143-169.
4. Thompson, P.B., *The Agricultural Ethics of Biofuels: The Food vs. Fuel Debate*. Agriculture, 2012. **2**(4): p. 339-358.
5. Pimentel, D., *Biomass utilization, limits of*. Encyclopedia of physical science and technology, 2001. **2**: p. 159-171.
6. Mohr, A. and S. Raman, *Lessons from first generation biofuels and implications for the sustainability appraisal of second generation biofuels*. Energy policy, 2013. **63**: p. 114-122.
7. de Beeck, B.O., et al., *Direct catalytic conversion of cellulose to liquid straight-chain alkanes*. Energy & Environmental Science, 2015. **8**(1): p. 230-240.
8. Vinke, I., *Development of a fuel mixture properties calculator with preparation for web-based implementation*. 2020.
9. vom Lehn, F., et al., *A property database of fuel compounds with emphasis on spark-ignition engine applications*. Applications in Energy and Combustion Science, 2021. **5**: p. 100018.
10. Jørgensen, H., J. Kristensen, and C. Felby, *Biofuels, Bioprod.* Biorefining, 2007. **1**: p. 119.
11. Szybist, J.P., et al., *What fuel properties enable higher thermal efficiency in spark-ignited engines?* Progress in Energy and Combustion Science, 2021. **82**: p. 100876.
12. Lehn, F.v. *Fuel Database, Fuel Property Modeling, and Fuel Selection*. Available from: www.itv.rwth-aachen.de/en/research/ongoing-research/fuel-database/.
13. Prugh, R.W., *Estimation of Flash Point Temperature*. 1973.
14. Hoang, A.T., et al., *Combustion and emission characteristics of spark and compression ignition engine fueled with 2, 5-dimethylfuran (DMF): A comprehensive review*. Fuel, 2020: p. 119757.
15. Hoppe, F., et al., *Tailor-Made Fuels from Biomass: Potentials of 2-butanone and 2-methylfuran in direct injection spark ignition engines*. Fuel, 2016. **167**: p. 106-117.
16. Çelebi, S., et al., *Operating range, combustion, performance and emissions of an HCCI engine fueled with naphtha*. Fuel, 2021. **283**: p. 118828.
17. Turner, J., et al., *GEM ternary blends: Removing the biomass limit by using iso-stoichiometric mixtures of gasoline, ethanol and methanol*. 2011, SAE Technical Paper.
18. murphy, M.J., *Compendium of Experimental Cetane Number Data*. 2004.
19. Serdari, A., E. Lois, and S. Stourmas, *Impact of esters of mono-and dicarboxylic acids on diesel fuel quality*. Industrial & engineering chemistry research, 1999. **38**(9): p. 3543-3548.
20. Lapuerta, M., et al., *Stability, lubricity, viscosity, and cold-flow properties of alcohol– diesel blends*. Energy & fuels, 2010. **24**(8): p. 4497-4502.
21. Kanaveli, I.-P., M. Atzemi, and E. Lois, *Predicting the viscosity of diesel/biodiesel blends*. Fuel, 2017. **199**: p. 248-263.

Acknowledgements

this paper was made possible by the support of the Energy Transition Fund of the Belgian federal government, within the project “Ad-Libio”, economie.fgov.be

Contact Information

Tom Robeyn
Department of Electromechanical, Systems and Metal Engineering
Research Team Sustainable Thermo-Fluid Energy Systems (STFES)
Campus UFO, Technicum Blok 4,
Sint-Pietersnieuwstraat 41, 9000 Ghent-Belgium
tom.robeyn@ugent.be