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Blending behavior of hydrocarbon and oxygenate molecules to optimize RON and MON for modern spark-ignition engines (SI)

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Abstract

Gasoline blending is known to be complicated, because individual gasoline fractions with different octane numbers, Research Octane Number (RON) or Motor Octane Number (MON) do not always blend linearly. Instead, they may blend non-linearly, in a synergistic or antagonistic manner. Even though RON and MON are regulated properties, linear and non-linear octane blending is not a broadly understood topic. The target in the developing process of a modern SI engine is to have 100% combustion efficiency which would lead to the reduction of hydrocarbon and carbon monoxide emissions. Therefore, the properties of gasoline, especially RON and MON, need to be optimized to ensure proper ignition in the engine and prevent harmful autoignition reactions.

There are hundreds of hydrocarbons in gasoline which have different octane numbers (ON). The explanations for these variations are the structural differences in hydrocarbon molecules that influence on their reactivity. For instance, longer n-paraffins have lower octane numbers compared to aromatics where electrons are delocalized around their ring which increases stability of aromatics and thus, ON. In this paper, we report and visualize qualitatively the octane blending behaviour of different hydrocarbon and oxygenate molecules to facilitate gasoline components mixing to produce high quality gasoline for clean combustion. The present study shows ethanol to blend non-linearly, but synergistically with paraffins and olefins, while the blending with aromatics is antagonistic. We also conclude that oxygenate molecules such as furans and cyclic ketones, blend synergistically with hydrocarbons. However, predicting the ON of end gasoline is challenging, as gasoline is not a blend of two components, but rather a blend of many isomers and functional groups. Therefore, in this study we highlight the need for more complex blending models than binary ones.

Introduction

Globally, the oil demand increased by 900 kilo barrels per day in the third quarter of 2019[1] that highlights the need of oil refining products even though, more sustainable raw materials have been proposed to substitute crude oil. Nowadays, world liquid fuels consumption is 100 million barrels per day[2] that is predicted to increase also in the next decades because of population growth and increasing urbanization[2,3].

Gasoline is one of the oil refinery products that covers over half of the profits of refineries in USA[4], otherwise in European countries, there is overproduction of gasoline[5]. However, this surplus gasoline can be exported and therefore, there is no immediate need for the cutting of gasoline production. Furthermore, the production of other refinery products such as diesel produces short carbon chain fractions suitable for gasoline.

There are hundreds of different hydrocarbons in gasoline such as isoparaffins, aromatics, and olefins but also shorter hydrocarbons like butane, and they all have different chemical structures. These structures cause challenges in the gasoline blending, especially in the octane blending, because they behave differently in the blends. Moreover, the production of more sustainable gasoline in the future could bring new molecules like ketones into gasoline blends. These molecules include oxygen which limit in gasoline is at maximum 3.7 wt%[6] nowadays. New oxygenate molecules are favoured because of their renewable raw materials, high Research Octane Numbers (RONs) and high sensitivities. Especially, the downsized and turbocharged spark-ignition (SI) engines require gasoline that has lower Motor Octane Number (MON) at a given RON[7]. However, there are still uncertainties in the blending behaviour of oxygenate molecules with fossil gasoline. Meanwhile, the target in the gasoline blending is always to produce high quality gasoline that needs to follow Fuel Quality Directive (FQD)[6], national laws and standards.

The properties of gasoline need to be optimized to ensure proper ignition characteristics and prevent the harmful autoignition reactions that might cause knocking. Knocking can destroy the engine that is managed by different engine strategies such as spark control and knock sensors[8] that belong to the most modern SI engines. However, these strategies may decrease the SI engine efficiency and its maximum power[9]. To prevent the knocking phenomenon, the properties of gasoline have a major role. Especially, RON and MON, are the properties that influence on knocking and by their proper balancing these challenges may be avoided.

RON and MON are not the easiest properties to control because they depend on the structure of molecules. For instance, Ghosh et al.[10] noticed long carbon chain to decrease the octane numbers, because then paraffins become more reactive. Also, naphthenes were found to have higher octane numbers than n-paraffins[11]. Furthermore, Bounaceur et al.[12] investigated the influence of the position of double bonds in olefins on the octane numbers. They noticed that olefins with more centrally located double bonds have higher RON due to the formation of tertiary carbon bonds. With the octane

number (ON) of each hydrocarbon it should be easy to calculate the gasoline octane numbers. However, the blending of these compounds together is not always linear necessitating the need for more advanced blending strategies.

Linear and non-linear octane blending is not a broadly investigated topic in the literature, even though ON is a regulated property. Therefore, this paper concentrates especially on the blending behaviour of different hydrocarbon and oxygenate molecules to optimize the production of high-quality gasoline. Ghosh et al.[10] investigated octane blending among similar hydrocarbon groups to prove their linear blending. In their study, they noticed paraffins to blend linearly with other paraffins and olefins with other olefins. Moreover, they discovered linear octane blending among naphthenes and olefins. However, blending structurally different aromatics have been noticed to yield a more complex blending behaviour[13] making it difficult to provide simple conclusion.

When blending hydrocarbons with structural differences, non-linear octane blending has been noticed. This blending can be divided into synergistic or antagonistic behaviour, where the former one was noticed[11] among ethanol and paraffins. Antagonistic blending was[14] noticed between aromatics and ethanol. It refers to blending a behaviour giving lower RON and MON than what would be linearly expected. Therefore, the octane blending among these components is more complex. Anderson et al.[15] noticed also nonlinear increase in the octane blending of alcohols and gasoline. However, they observed that use of molar concentrations instead of volumetric concentrations reduced the nonlinearity.

There are works of blending behaviour trends between hydrocarbons and the most used oxygenated hydrocarbons, ethanol and ethers in the literature. However, the previous studies do not provide a clear explanation why nonlinear blending occurs and which factors affect to that. Moreover, a detailed understanding of phenomena that are behind the blending behaviours such as intermolecular interactions and molecules' functionalities are not identified explicitly. Therefore, there is a huge need to further understand of these phenomena behind blending behaviours in more detail. For the authors' knowledge, there are only few works of blending behaviour trends among future oxygenated molecules, such as other alcohols or ketones.

There are several compounds that could increase octane numbers such as organometals and organic compounds, while the former such as tetraethyl lead (TEL) has been disabled because their harmful effects to the health and incompatibility with the catalytic converters in the vehicles[11]. Nowadays, oxygenate molecules such as ethers and alcohols are the most utilized octane boosters. They can be produced from non-fossil raw material streams and therefore, will become more appealing in the future gasoline blends. This paper focuses on different oxygenates from new raw material streams such as cyclic ketones and esters to investigate their impact to the gasoline blending. Therefore, this study provides also an outlook for the intermolecular bonding between different molecules. However, there are also problems in the use of these new oxygenated molecules regarding the engine compatibility, groundwater issues and gasoline storing.

The use of methyl tert-butyl ether as octane booster has been banned in California due to its leakage from underground storage tanks into the groundwater[16]. In addition, ethers and alcohols may cause vapor lock in the engine due to their high vapor pressures and low boiling points [17]. Alcohols are good solvents which increase their probability to cause corrosion at higher concentrations in some engine parts, for instance in the cylinder walls. However, gasoline with ethanol content below 10 vol% has not been noticed to have these problems [18]. While ketones may cause problems with seals during gasoline storing because their high polarity. Kass et al.[19]noticed cyclic ketones to cause volume swelling of elastomers of seals. These all compatibility aspects of oxygenated molecules need to be considered carefully before their larger adoption.

In this paper, we summarize the octane blending behaviour of different molecules from the several literature sources. With them we point where more blending research is needed to facilitate gasoline components mixing to produce high quality gasoline. As red circle in Figure 1 presents, the target of this study is to define possible blending components and recognize their behaviour in binary blends according to previous studies.

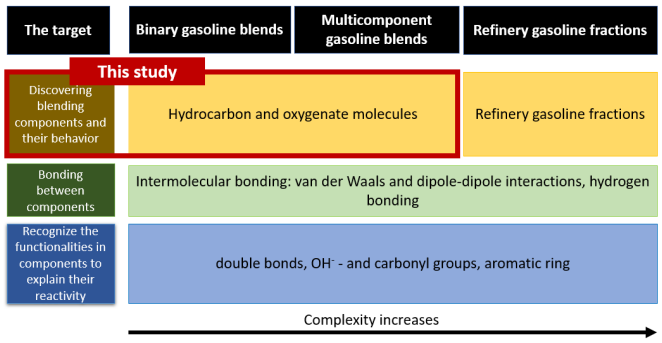


Figure 1. Visual presentation of the target in this study.

The before mentioned studies have focused solely on the blending behaviour of two molecules. Therefore, the influence of several molecules' presence in gasoline on their octane blending is investigated from available literature sources as red circle in Figure 1 indicates.

Blending data

In this paper, the qualitative octane blending behaviour of different hydrocarbon and oxygenate molecules is obtained from available literature sources[10,13,14,20,21]. In the case of linear blending of gasoline fractions, RON or MON are easy to forecast by Equation 1 which presents gasoline blend including three fractions.

$$RON_{gasoline} = x1 * RON_1 + x2 * RON_2 + x3 * RON_3 \qquad (1)$$

, where x1 is the share of fraction one in gasoline blend and RON_1 is its RON.

In the literature sources, the blending behaviour of molecule groups has been investigated in laboratories by forming binary blends of individual molecules[10] which RONs are then qualitatively compared to linearly assumed RON with the same principle as Equation 1 presents.

Foong et al.[14] investigated the blending of toluene with different fractions to blend of iso-octane and n-heptane to recognize its octane blending behaviour. In one literature source[13], gasoline fractions; isomerate, reformate and alkylate have been studied by calculating their RONs in the study designed model and investigating molecular

composition of gasoline fractions. Da Silva Jr. et al.[21] measured RONs of gasoline surrogate/ethanol blends with the equilibrium fuel level procedure. This method uses two reference fuels with a known RONs to estimate the gasoline surrogates/ethanol fuels. In their study, olefins were noticed to blend with ethanol in the synergistic manner in RON conditions.

Farrell et al. [20] reported the behaviour of oxygenate molecules with hydrocarbon mixture. The studied molecules do not exist in conventional fossil gasoline but are viable options in the future. In theory it is well known that molecules' individual RON and MON values have different effect on the mixture octane numbers as presented in Figure 2 where the blending is presented to be linear or nonlinear; synergistic or antagonistic. This study applies in the later parts, the octane scale for RON from 95 onward and for MON from 85 onward. We chose these scales based on the FQD[6] which defines the lower limits for the gasoline octane numbers.

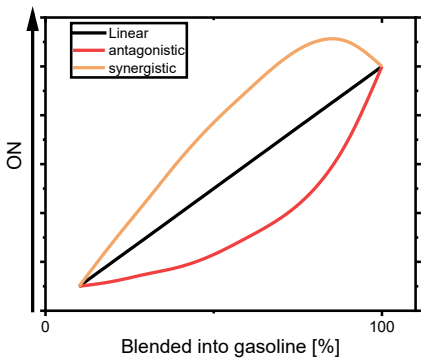


Figure 2. Different blending behaviors of ON for gasoline fractions: blending can be linear or nonlinear: synergistic or antagonistic.

Normally, the ON calculations are not that straight forward as Equation 1 and black line in Figure 2 shows because the impact of ONs of individual molecules might be higher or lower than the fraction of molecule tells. This octane blending is called nonlinear and it can be divided into synergistic or antagonistic as shown in Figure 2. The synergistic octane blending of gasoline molecules refers to behaviour that produces higher ON for the blend than linearly assumed. While antagonistic octane blending produces ON for the gasoline blend that is lower than linearly assumed.

Hydrocarbons and oxygenates

In this paper, we focus on four hydrocarbon groups that form gasoline and in addition, possible oxygenate molecules that are applied already or are viable future gasoline molecules. Hydrocarbons that are present in gasoline are paraffins, olefins, aromatics and naphthenes.

Paraffins are saturated, straight or branched chain hydrocarbons that gasoline usually contains 30-60 vol%[22]. Among paraffins, branched paraffins, also called isoparaffins are more desired than straight chain paraffins, n-paraffins, due their higher RON. In addition to n-paraffins and isoparaffins there are also naphthenes, cyclic paraffins, in gasoline. Naphthenes are not as common hydrocarbons in gasoline than iso- and n-parafffins, but their structure is desired because it can be dehydrogenated into aromatics in gasoline upgrading units. Olefins are other hydrocarbons that can be found in gasoline which contain normally one double bond and have higher octane numbers than paraffins. Dienes are olefins that have multiple double bonds and are toxic, but they are hydrogenated by selective hydrogenation and thus, their content in gasoline is small. FQD limits olefins to 18 vol%[6] in gasoline.

Aromatics are molecules that consist of a benzene ring and their amount is limited to 35 vol%[6] due to their carcinogenic nature. Benzene itself is limited to 1 vol%[6] in gasoline to decrease its harmful health effects. However, aromatics have highest RONs and high sensitivities among hydrocarbons and thus, they are widely used in gasoline. There are also possibilities to find polyaromatic hydrocarbons such as naphthalenes in gasoline which could cause soot in SI-engine[22]. Also, mono-aromatics cause emissions due to their incomplete combustion.

There is increased interest to decrease gasoline carbon footprint and therefore, the addition of oxygen containing molecules such as renewable based ethanol is desired[23]. The content of oxygen in gasoline is regulated to maximum 3.7 wt%[6] that also restricts the blending of ethanol to gasoline up to 10 vol%. The benefits to gasoline from ethanol are its ability to increase RON and engine efficiency[8]. In addition to hydrocarbon molecules, in this study is presented the blending of other oxygenate hydrocarbon molecules to study the blending behaviour of ketones, furans and esters.

Ketones have one oxygen attached with a double bond and they have been noticed to be viable molecules to increase the gasoline RON[24]. In this study, we focus on the octane blending of cyclic ketones with hydrocarbons. There are also furans among oxygenates that should be considered due to their high knocking resistance and especially, methyl- and dimethylfurans have been noticed to decrease acetaldehyde and formaldehyde emissions[25] compared to fossil-based gasoline. Fourth oxygenate molecule that is considered in this study is ester which contains two oxygen; one attached by double bond and other by single bond. In the previous study have been noticed esters to reduce Reid vapor pressure (RVP)[26] that could provide low RVP for gasoline in regions where temperature is high. As renewable or waste raw materials could be utilized as raw materials for all these oxygenate molecules, this would significantly lower the gasoline carbon footprint.

Results

There are several upgrading units in the refineries that produce gasoline fractions which are then blended together to form gasoline. Those upgrading units modify hydrocarbons by isomerization, hydrogenation, aromatization and cracking and thus, the upgraded gasoline blending fractions differ each other by their chemical structure. Due to those chemical differences, also their RONs and MONs have variations. Figure 3 presents RONs and MONs of gasoline molecule groups concerned in this study by one representative of each group.

Figure 3 shows clear differences among RONs and MONs between different gasoline molecules. Therefore, there are several methods to upgrade gasoline to produce all these various chemical structures and ensure the required ON. However, the high ONs of individual gasoline blending molecules do not guarantee a high ONs for gasoline blend due to possible nonlinear blending that challenges the forecast of the final gasoline ON. Thus, now when oxygenated molecules from the new raw material streams are emerging into the refineries, it is vital to better understand the effect of functional groups in these molecules.

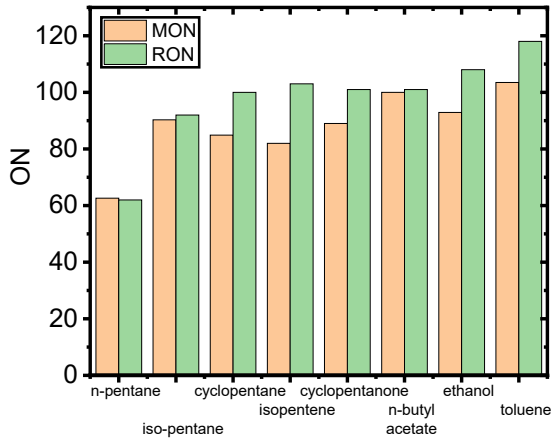


Figure 3. ON varies among hydrocarbon molecules and ethanol depending on their chemical structure. Data from Ghosh et al.[10] and Gaspar et al[26].

Binary blends

In this section, we present the octane blending behavior of individual gasoline molecule groups and their effect on the RON of binary blend, they are visually presented in Table 1 where the different colors indicate the blending behavior.

Table 1 summarizes the octane blending behavior of different hydrocarbon and oxygenate groups by showing which hydrocarbon and oxygenate molecules blend together linearly and which synergistic or antagonistic according to their RON and MON. However, the MON blending is not covered between all molecules in the literature. Table 1indicates that by separating those molecules with dashed lines.

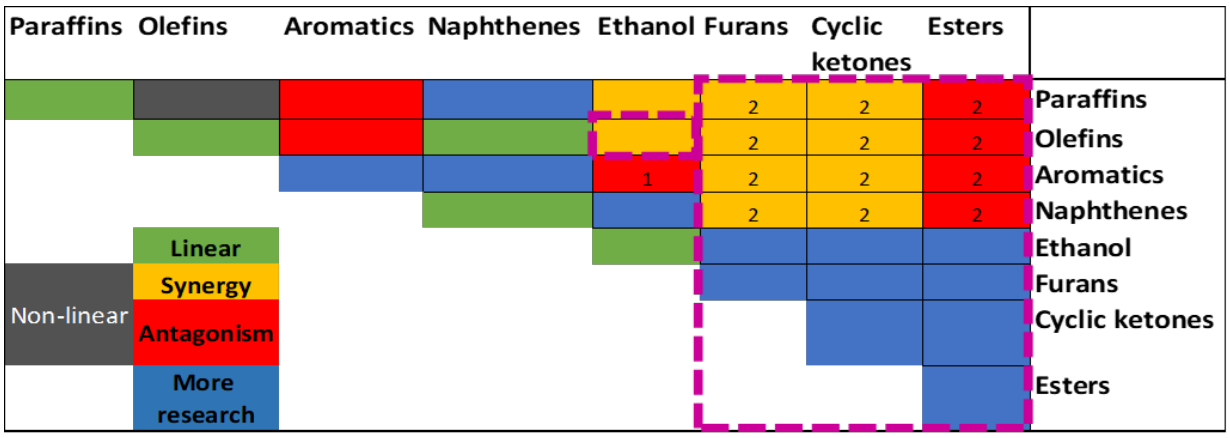
The linear blending is indicated with green color, and the nonlinearity with grey. The nonlinearity is further divided to red and yellow to show the antagonism and synergism octane blending, if known. There is also blue color in Table 1 that indicates inconsistency in the studies or entirely lacking data and implies that the further research is needed.

What can be notice from Table 1, is the scarcity of the green color that indicates octane blending to be mainly non-linear that also creates challenges to refineries. This confirms that if ON predictions are based on the linear models, they are not enough accurate and more advanced models are needed. Nonetheless, those models have worked because there is also linear octane blending between similar hydrocarbon groups (paraffins). However, the blending between different aromatics is not defined to be linear and still needs further research. In the future, this type of compounds will be present at high concentrations in these blends that underlines the urgency to build more complex models.

Table 1 shows naphthenes to blend with olefins linearly even though their chemical structures distinguish from each other. This could be due to a possibility to naphthenes also contain double bonds because it is seldom specified in studies. However, the amount of naphthenes is low in gasoline that could be change in the future due to their high RONs and higher sensitivities than for instance paraffins have.

In Table 1, the nonlinear octane blending is shown with grey color if it cannot be to specify to synergistic or antagonistic. That is the case between olefins and paraffins which blending results ON that differs from linearly assumed. However, there are yellow and red color in Table 1 that indicates the founded synergism and antagonism between hydrocarbon and oxygenate molecules as was founded also other study[20].

Table 1. The octane blending between hydrocarbon and oxygenate molecules can be linear (green color) or nonlinear (grey color). Furthermore, nonlinear octane blending can be divided into synergistic (yellow color) and antagonistic (red color). Visualization based on[10, 13, 14, 20, 21]. There is also blue color that indicates the lack of knowledge of octane blending among some molecules. Behavior of molecules with dashed lines indicates the non-recognized MON blending between specific molecules.



To help to understand visually the nonlinearity between different molecule groups, Figure 4 visualizes qualitatively RON blending of paraffins between ethanol and between ethanol and aromatics. Figure 5 illustrates qualitatively the MON blending between the before mentioned molecules. As Figure 4 and 5 shows the blending of ethanol and paraffins is synergistic both in the RON and MON manners that is suggested also in previous studies[11,21]. Whereas the RON blending of aromatics is antagonistic with paraffins, olefins and ethanol as also founded in other studies[13,14].

Figure 5 shows MON blending between ethanol and aromatics to be antagonistic and between ethanol and paraffins to be synergistic. In Table 1, the MON blending between olefins and ethanol cannot be defined synergistic according to MON. The magnitude of the antagonistic and synergistic phenomena between molecules cannot be quantified detail that is illustrated also by dashed lines in Figures 4 and 5.

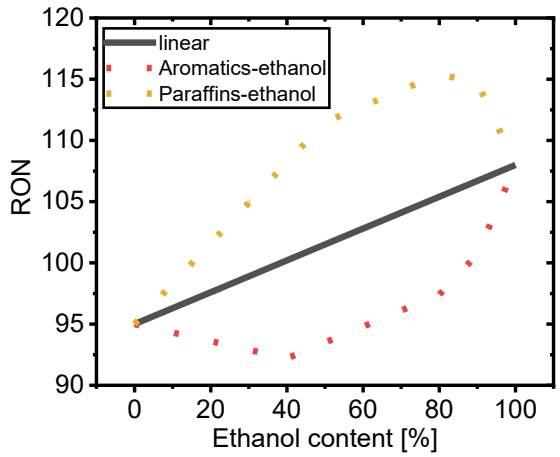


Figure 4. The visualization of behavior between paraffins and ethanol and aromatics and ethanol in binary blend and its influence on RON[11].

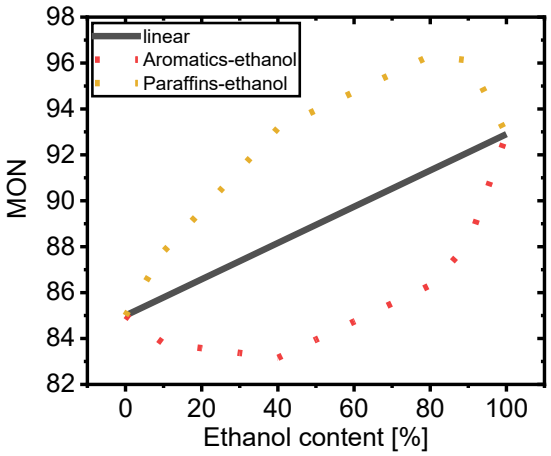


Figure 5. The visualization of MON blending between ethanol and aromatics and between ethanol and paraffins[14].

However, the octane blending between aromatics and ethanol is still more complicated because methyl groups in aromatic ring could reduce the antagonistic blending by turning it more linear. The more there is methyl substituents in aromatic molecules the less reactive they are that indicates their high RON which may influence on gasoline blend as well by increasing its RON.

Oxygenated molecules are also part of Table 1 where they show nonlinear RON blending with hydrocarbons. For instance, cyclic ketones and furans blend synergistic with hydrocarbons, while esters are noticed to blend antagonistic as shown in Figure 6. The dashed lines in Figure 6 predicts the non-quantified nonlinearity between different oxygenated molecules and hydrocarbons. Farrell et al. [20] presented nonlinear blending of oxygenates in RON, but they did not provide information how oxygenate molecules behave in the blending of MON.

These oxygenate molecules have high RONs and sensitivities, despite esters that have low sensitivity as Figure 3 shows. Moreover, oxygenate molecules decrease emissions in SI engine and increase oxygen content in gasoline. This reduces flame temperatures during combustion that reduces the heat losses[27] in SI engine. It has also been found that in gasoline with oxygenated molecules there is large production of combustion products and high cylinder pressure[27] whereas, the lower heating value of gasoline would decrease due to oxygen in molecules.

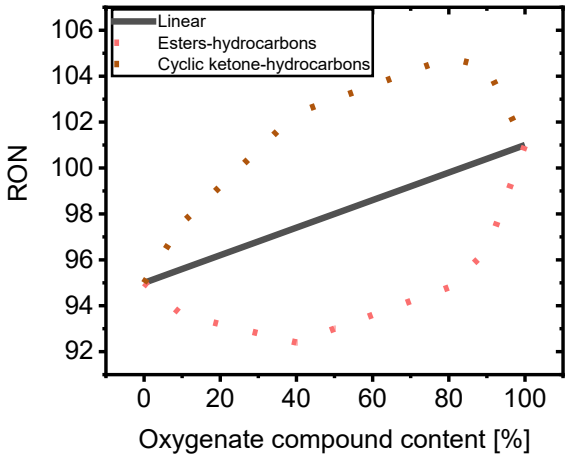


Figure 6. The visualization of mixing cyclic ketones and esters with hydrocarbons and its effect to RON [20].

For many of molecule groups, there is an idea of octane blending behavior (Table 1) but still the blue color covers a large amount of Table 1 and large research effort is still required to better understand the behaviors of these different molecules. The octane blending of paraffins is noticed to be clear with most molecules but with naphthenes no clear correlation has been reported. As previously mentioned, naphthenes can contain double bonds or be saturated. Therefore, their octane blending with paraffins can be predicted linear if there are no double bonds in naphthenes structure, but it is important to remember that cyclic structures are more stable which might have an influence on blending.

The octane blending between aromatics and naphthenes is more complicated and could be predicted non-linear due to their different structures. There are cyclic structures in both molecules but the delocalized electrons in aromatics increase their stability versus naphthenes' structure. This is also shown in Figure 3 where cyclopentane has lower ONs than toluene that refers to its higher reactivity.

The part in Table 1 that needs more research is obviously oxygenate molecules due to their new functionalities in gasoline blends. Nevertheless, some assumptions have been already found[20] between hydrocarbons and oxygenate molecules such as their synergistic RON blending as shown (Table 1). Those hydrocarbon groups are not specified and, therefore there might be variations between aromatics and paraffins octane blending with furans or cyclic ketones.

One of the differences between oxygenate and hydrocarbon molecules is their intermolecular bonding that varies according to the functionality in molecule. In gasoline, hydrocarbons are interacted to each other via van der Waals forces, while the addition of alcohols and ketones brings new interactions; hydrogen and dipole-dipole bonds. Former could be between alcohols and the latter interaction occurs between carbonyl groups that are present in ketones. These new intermolecular interactions might have a boosting or reducing influence on the octane blending between oxygenate and hydrocarbon molecules in gasoline that we need to consider in the future.

Multicomponent blends

In the previous section, we evaluated the octane blending of two molecule groups at once. However, there have been reported clear difference in octane blending between two molecules when there are various molecule groups present in blend[28]. Therefore, this section shows how gasoline octane blending varies with in multiple molecules blend.

Table 1 considers the octane blending between two molecules that does not consider blends in which are multiple molecular groups. Weber de Menezes et al. [28] noticed that ethanol increased ONs more in iso- and n-paraffinic rich gasoline blend than in aromatic blend as it is also illustrated in Figure 7. Weber de Menezes et al. found the increase of RON to be higher when ethanol is added compared to the increase of MON of the blend as Figure 7 also illustrates. They explained it with the difference of the test conditions of RON and MON. Ethanol increases MON of the blends almost regardless of the composition of base gasoline. The dashed lines in Figure 7 illustrate that the nonlinearity cannot be quantified explicitly.

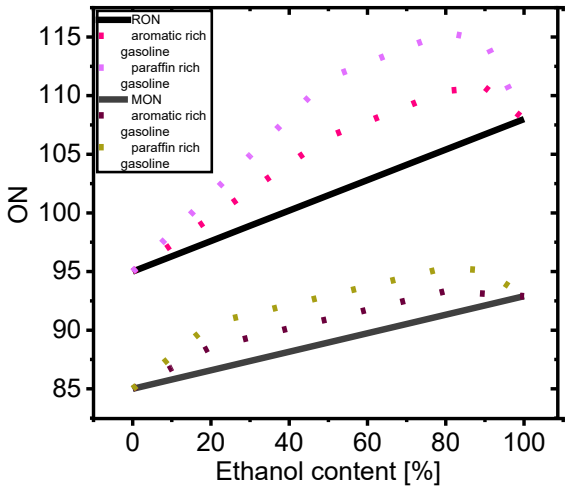


Figure 7. The visual comparison of ethanol influence on paraffin rich gasoline blend and aromatic rich blend [28].

However, they also reported some synergism effect when ethanol was added into the aromatic rich gasoline blend even though aromatics and ethanol was noticed to blend antagonistic in Table 1. Figure 7 shows that the octane blending behavior can change totally by adding other molecules to binary blends. However, the behavior of molecules in binary blends is useful to recognize first to predict their blending in multicomponent blends.

Based on the visualization in Figure 7 and Table 1 the estimation of blending ethanol to olefin rich gasoline could also produce higher ONs than its blending into aromatic rich gasoline, because olefins blend synergistically with ethanol like paraffins. While the influence of ethanol addition into blend where are other oxygenate molecules is not researched and will need deeper understanding.

In addition to ethanol, other oxygenate molecules should be investigated in multicomponent blends as well to find out if there are similar trends. For instance, Table 1 predicts esters to blend with hydrocarbons antagonistically but if the content in some hydrocarbon groups is increased, could blending be synergistic. This question could be solved with further research of interactions between hydrocarbon and oxygenate molecules in gasoline.

Conclusions

This study presents gasoline molecules behavior in binary and multicomponent blends to produce high quality gasoline for modern SI engine. It is important to recognize these behaviors between different molecules because they influence on the gasoline properties and especially octane blending. We summarized octane blending of hydrocarbon molecules with the available literature sources. Also, the available octane blending data of oxygenated molecules with hydrocarbon molecules is utilized to highlight their influence on blending. These molecules could decrease gasoline emissions, but they also may cause compatibility problems in the engine and during gasoline storing.

The octane blending is divided into linear and nonlinear blending; while the nonlinear blending can be further divided into synergistic and antagonistic blending. Linear blending is reported among same molecular groups however, aromatics are noticed to be an exception in this due to their complex structure. In addition to blending behavior between aromatics, ethanol blends in an antagonistic manner with aromatics and synergistic with paraffins. However, this blending reaches linear manner when the amount of methyl substituents increases in aromatic ring.

This study presents also how the octane blending changes in the multicomponent blends compared to binary blends. Octane blending of ethanol was synergistic with two different gasoline blends where aromatic and paraffin contents vary. This finding shows different behavior between ethanol and aromatics than in binary blends where they are blended antagonistically. Therefore, the presence of other molecules in the blend is necessary to take into consideration when planning blending.

In future studies, the focus will be on the octane blending of sustainable bioderived oxygenated molecules with hydrocarbon molecules due to their potential to produce more sustainable gasoline for SI engines. Moreover, oxygenate molecule have different intermolecular interactions than hydrocarbons due to oxygen in their structure. These variations in the intermolecular interactions needs to

be considered in gasoline octane blending where they might have synergistic or antagonistic effect to ONs.

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Abbreviations

FQD	Fuel Quality Directive
MON	Motor Octane Number
ON	Octane Number
RON	Research Octane Number
RVP	Reid Vapor pressure
SI	spark-ignition
TEL	tetraethyl lead