Possibilities of Ethanol replacement within regular blends of gasoline with different biofuels

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Abstract:

This study aims to find the solution to whether or not novel biofuels (such as those highlighted in the Co-Optima program from the U.S. Department of Energy) can replace ethanol in mainstream vehicles by thermodynamically saving energy from production to combustion. Throughout research and investigation, it has been proven that fuels such as butyl-acetate and 2-methylfuran can be more thermodynamically efficient from processes regarding production to combustion, because of the extremely high enthalpy capacities that the production of these fuels could potentially take before matching the amount of energy that the production of 1 gallon of ethanol requires as compared to the rest of the biofuels. Limitations of the gasoline engine only can support a certain density which if passed can cause problems regarding clogging in fuel lines, incomplete combustion, and stalling. Therefore, only a 7-93 butyl-acetate gasoline blend and a 5-95 2-methylfuran gasoline blend can be used without needing significant modifications to the gasoline engine to ensure the problems previously mentioned do not occur. Cantera software was used to generate data regarding biofuels, which helped better understand the amount of energy used while the combustion process took place within a gasoline engine. The limited amount of biofuels that can be used in these blends poses a problem with efficiency regarding how much gasoline can be saved. The efficiency of the gasoline engine had to be 2x-3x better while using biofuels (regarding pre-ignition times and lower heating values), as compared to ethanol, which it is not. Although these fuels are thermodynamically more efficient from production to combustion, the practicality aspect of these fuels cannot permit the use of alternative blends in gasoline engines.

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1. Introduction:

With ongoing research on biofuels and alternatives, many new fuel sources have been discovered to have the potential to be better than that of current solutions which include a blend of ethanol and gasoline. Recent reviews have been published evaluating the effectiveness of replacing gasoline fuels entirely, or even switching to a different mechanism that essentially runs our vehicles. However, research conducted by the U.S. Department of Energy reveals that there are over 200 million registered gasoline cars [1]. Although other fuel systems have been growing (in California particularly), and are great for the environment, the offset of gasoline cars or having to convert them entirely just shifts the damage from fuels causing it to the cars because they have to be scrapped. The U.S. Department of Energy (DOE) knows this concern as well, and they have been continuously researching alternative fuels as well [2]. One of the main focuses of DOE's research also lies in replacing ethanol as a blend within gasoline, something which is the main focus of this article. The main goal of this co-optima program is to "maximize vehicle performance and efficiency and leverage domestic fuel resources". As highlighted in DOE's research, there are many different types of groups consisting of multiple different fuels all of which are being investigated to see if they could be more useful/efficient in modern gasoline engines.

As more advanced and cleaner energy sources are still under development and aren't ready to be used in vehicles all over the US, so ethanol (E10) has been referred to as the replacement fuel for gasoline but not an alternative one by energy.gov [3]. The problem with ethanol is that it has a relatively low energy content (66% of that of gasoline) [4] which when applied with higher and higher blends, causes higher heating values leading to an inefficient engine. Ethanol isn't going to be able to replace gasoline simply because of its weak energy sources, such as only having 66% of the energy of gasoline, or even being of a greater density. Another reason ethanol cannot replace gasoline on its own is because of the problems with engines not being able to take E100 or even E85. As mentioned by the U.S. Department of Energy, ethanol's use of, "Special lubricants may be required". Therefore it is currently being used as a blend in gasoline, to make it cleaner for the environment to use as a fuel, and not have a majorly significant downside of the power loss as compared to using ethanol as a whole solution.

One of the current solutions we have is to replace ethanol within the gasoline blend with another fuel. Engines have already reached the maximum amount of efficiency they can through the use of modern technology and the restrictions being placed by the US and EU based on climate change. Replacing ethanol could result in a better, more probable solution to fighting the waste of energy at this time. Ethanol is not only inefficient when compared to gasoline (.66 gasoline gallon equivalent for ethanol to 1 gasoline gallon equivalent for gasoline), but the production of ethanol requires a decent amount of energy as well, 40 MJ per gallon produced [5]. Can other biofuels be more efficient to be produced thermodynamically from start to finish?

The goal of this study is to explore the possibility of implementing experimental biofuels as showcased by DOE's Co-Optima program into gasoline or even gasoline/ethanol blends. Another major point of this study is to find whether or not alternative biofuels such as Butyl-Acetate (BA), and 2-Methylfuran (2-MF) are more thermodynamically efficient as compared to ethanol from production to combustion in a gasoline engine. BA and 2-MF have been previously used in industries for various reasons. Most notably, BA is used for things such as nail polish remover, perfumes, and oils [6], and 2-MF is used for items such as paint [7]. These chemicals have been produced for various uses, and with the added potential of being used as fuels, they could benefit from wider production. Nonetheless, if these fuels have favorable properties that could replace ethanol in gasoline cars, this would be a major benefit as it would save so much energy by being more efficient, and by requiring less energy to be produced.

2.1 Overview of the Processes and Previous Work:

Throughout this study, the optimization of software, and the review of different research papers will be executed to generate and gather data. This data will later be used to compare 2-MF and BA to ethanol, answering the question of whether these different fuels are better replacements or not. The study has managed to implement different sources of information, mostly being published after 2021 to find relevant, and the newest information on technology advancing this field. Websites were also used in gathering data, but they were all reputable government websites (.gov). The main reason these websites were used was to gather data that has already been established, such as data about fuel properties, handling, etc.

There have been many conventional methods of producing 2-methylfuran and butyl acetate that have existed for a very long time, they just haven't been industrialized on a large scale, CSTR tanks for butyl-acetate for example [8]. This study focuses on modern production methods for the production of butyl-acetate and 2-methylfuran. This doesn't apply to ethanol because ethanol has been industrialized already for a long time. Ethanol has a very specific process turning it from corn to fuel, so even older articles stay relevant in terms of the latest production methods for ethanol.

2.2 Overview of Mechanisms

This study implements the use of Cantera, [9] a chemistry simulation software. Cantera itself can't run simulations on biofuels, therefore we are going to have to use mechanisms. The mechanisms are chemical reactions that have been captured in code to theoretically produce different results when mixing up the inputs. The purpose of using such mechanisms is to prove the efficiencies of biofuels over ethanol. Only two mechanisms will be used in this study to gather data, that being mechanisms from Creck Dynamics Explosion Lab [10], and a mechanism based on a study conducting experiments on butyl-acetate [11]. These simulations will be used to study lower heating values (LHVs) of fuels and pre-ignition delay timing for these fuels. The lower the LHV, the better it combusts, meaning a higher Octane Rating, meaning better efficiency for your engine. The aim of this study is to find if some biofuel is more thermodynamically efficient than something else, and LHVs are a key aspect in finding out whether or not biofuels are more efficient or not. Simulation of blends between gasoline and ethanol will be done, which will be compared to the blends within BA and 2-MF, explaining whether or not biofuels such as these will be able to replace ethanol in terms of energy use at combustion.

3. Processes of Fuels

This section of the study will mainly focus on the production and the combustion of the different biofuels involved in the process, going in-depth as to what was done to find the data generated and in-depth analysis of how the production methods vary while comparing them to one another. Criteria have been set as discussed in the previous section, maintaining consistency and accuracy within the study. The goal of this section is to find out whether or not energy is saved throughout the production methods of 2-MF and BA while comparing it to that of Ethanol. This process will also be done to the combustion sections of the fuels as well.

3.1 Production of Biofuels

There have been many different ways to produce novel biofuels such as 2-MF and BA throughout the past. There have been many recently proposed solutions for producing these sorts of fuels, but they haven't been industrialized as the production methods are heavily experimental. Using the conventional methods for producing these fuels [12], would result in objectively higher energy usage. Using experimental methods to produce these biofuels would result in a greater energy savings method, and would be way easier to implement, as they use the most recent technology for making these fuels.

The main production method for ethanol is the least complex, turning corn into fuel which will be used as an additive into gasoline [13]. Because these methods have been industrialized for as long as ethanol has been produced, there have been limited/if any changes made to the production to further optimize its output. This means that methods and quantities of energy related to ethanol will be the same whether the process was taking place in 2006 or even in 2024 [14]. The process of turning corn into ethanol has many different steps. Firstly, there needs to be a reliable source of corn to start the process. The dry-milling process can begin after corn has been obtained. Milling of corn separates corn into multiple different pieces, some of which are important for the production of ethanol, and the rest which aren't. In this case, dry-milling breaks corn into corn starch, which is what ethanol production needs [15]. After milling is liquefaction, which makes the corn starch into a slurry. The slurry produced through liquefaction needs to be cooked at 90-150 C to reach the right properties for the next step. Saccharification is a process where the cooked slurry is constantly mashed. Saccharification separates sugars from the ones that can be fermented, from the ones that cannot. After saccharification, fermentation takes place. Fermentation is the biggest step in making ethanol, as fermentation is the step that allows alcohol (or in this case ethanol) to be produced. Dehydration distillation is the last step, which separates the solvent from the solution leaving the entire process with ethanol. Denaturation happens within those steps, which means that ethanol is an alcohol that a human cannot consume [16]. After all of these steps, ethanol is finally produced. But what about the energy aspect? According to a study conducted in 1995, ethanol requires around 40 MJ of energy to produce 1 gallon, and this does not include the aspect of producing the crops. Other biofuels need to have a lower amount of energy used while the fuels are being produced.

As for the production methods of 2-MF and BA, it gets a little more complicated. This is because these biofuels are mainly produced from other chemicals, not from some source that is readily available such as ethanol. For that reason, this study is not going in-depth as to how the ingredients were sourced out, only focusing on how these biofuels are being produced. This also explains why the production of corn was not included in the total energy used to produce 1 gallon of ethanol. As mentioned previously in this study, BA and 2-MF have experimental methods being implemented to produce these fuels because these fuels aren't readily industrialized. Using the latest experimental technology, there have been some promising ways to produce 2-MF and BA through the use of complex machinery. That being a Membrane Reactor and a Hydrogenolysis Machine. When talking about the production of BA, it uses a membrane reactor to be produced [17]. The membrane reactor works on LeChatalier's Principle, which mentions what happens if an equilibrium of a chemical reaction is shifted, and how that reaction reaches equilibrium again. In this scenario, n-butanol and acetic acid are the reactants, whereas butyl-acetate and water are the products. The membrane reactor constantly removes products through a semipermeable membrane (hence the name Membrane Reactor), which forces the equilibrium in the chemical equation towards the right, causing the reactants to make more products to compensate for the originally missing product. The result of this process is supposedly 99% efficiency, meaning 99% of the reactants will turn into the product. Not only is this process more efficient than that of using CSTR machines, but they are also more energy efficient. As for 2-MF, it uses a different technology on its own. It requires a hydrogenation machine, which is something where the hydrogenolysis process takes place, the main method required to make 2-MF [18]. The entire point of this process is to make sure that the production of 2-MF is quick, as using hydrogenolysis machines without catalysts could pose dangers as hydrogen transfer isn't a particularly safe process. Hydrogen needs to be transferred to make 2-MF. The entire process begins with reacting Furfural with iso-propyl alcohol, which gives us the products of furfural alcohol, and acetone. Out of these chemicals, furfural alcohol will be reacted upon again with isopropyl alcohol to make 2-MF. The reason these biofuels mainly have a one-step process is because these fuels don't have a particular substance that can be reacted upon multiple times to make these fuels. For example, ethanol is made from corn, which is heavily reacted upon, but these different fuels use different chemicals, and make chemical reactions for the production of these biofuels.

Since the production methods are heavily experimental and haven't been industrialized, there isn't a specific way to determine the amount of energy being used to produce these biofuels aside from estimation. Energy contents were not provided by the sources in which these experimental methods were being carried out. To estimate the energy amounts being used throughout the process for the production of 1 gallon of a certain fuel, there need to be some parameters set. There will be assumptions of 70% efficiency unless previous studies mention any greater efficiency (such as the reverse membrane reactor article which proposed a 99% efficiency). The density of these fuels will be used, along with the product molar mass to make proper estimations as to how much energy is being utilized to produce 1 gallon. Enthalpy change will be assumed to be X because the enthalpy amounts of these fuels aren't provided within their production methods. This means that we will find a value of enthalpy, which if the production methods do not exceed, the amount of energy used to produce 1 gallon of ethanol will be similar to 2-MF and BA. The Density of BA and 2-MF are .88g/mL and 0.9 g/mL respectively. The molar mass of these products is 116.16g/mol (BA) and 82.10 g/mol (2-MF). [19] [7]. This information will be used to approximate energy use through different calculations. Firstly, to find the mass of the product requires multiplying 3785 mL (amount of liquid in a gallon) by the certain fuels' density. That number then needs to be divided by the molar mass of the product, to calculate the amount of moles within a gallon of a certain biofuel. That number then needs to be multiplied by the enthalpy change per mole of that specific biofuel. Finally, that number is divided by the efficiency of the machine, resulting in the total amount of product produced. Given these scenarios, the enthalpy can be as low as -600KJ/mol for 2-MF to even match 1 gallon of Ethanol produced. That number is likely to be lower than that amount, meaning the production method for 2-MF saves more energy than that of Ethanol given its enthalpy is more than -600KJ/mol. But what about BA? Given the different 99% efficiency provided in the article, the equation stays the same, except for the fact that the density, and the molar mass change as well. Doing the calculation provided above results in the enthalpy being able to be as low as -1300KJ/mol to produce 1 gallon of BA which would be equivalent in terms of energy to that of ethanol. These values were generated based on previous studies regarding production methods of fuels, as mentioned in the previous passage. Butyl-acetate and 2-MF have greater efficiency in terms of energy used to produce 1 gallon of these biofuels. To match the energy required by ethanol, the enthalpy of these fuels during the reaction has to be extremely low, which is most likely not the case. So far, biofuels such as butyl-acetate and 2-methylfuran have the edge in terms of energy used while the fuels are being produced.

3.2 Data of Biofuels

The most important part of figuring out whether or not a particular fuel can replace Ethanol in the real world is through the testing of the combustion process. Before fuel can be combusted within an engine, it has to be produced and then stored somewhere. This study already investigated production methods, but what about storage? Because these fuels have boiling points similar to that of gasoline, the temperature doesn't have to be regulated to a certain degree. Storage doesn't play a factor because it simply uses no energy. The same goes for transport as well, because the transport of fuels will stay the same, either through trains or tanker trucks. If anything, the energy usage of transporting BA and 2-MF may be slightly higher because they are heavier fuels, but the difference is negligible.

The data used within this study consists of certain values which include lower heating values (or LHVs) of these fuels, along with the ignition delay data timing for how effective these biofuels are in a 4-stroke gasoline engine. The purpose of finding LHVs and Pre-Ignition Delay data is to find whether or not Ethanol is more efficient in combustion as compared to 2-MF, and BA by determining which fuel has the lower LHVs, and what fuel has a better pre-ignition time. The lower the time, the more effective the engine is when reacting with the fuel. Furthermore, data collection with different stoichiometric ratios of gasoline and biofuels will be conducted, which then will later be evaluated in terms of what fuel ratio is perfect for use in gasoline engines.

The data of LHVs were produced using the Cantera software in Google Colab, through the use of many different mechanisms such as a mechanism for Butyl-Acetate provided by MIT, and a 2-Methylfuran Mechanism provided by Creck Dynamics Explosion lab. Through the usage of the Cantera code and different mechanisms provided, LHVs were able to be calculated for these different fuels. Pressures and temperatures were adjusted to mimic that of an engine, both of which are supposed to be conditions just before combustion takes place in a 4-stroke engine. To be more specific, the temperature was set to 673 kelvin, and the pressure was set to 689476 pascals. Mole fractions of fuels were set to be 1 for biofuels and 0 for gasoline, and the pure LHVs were produced for these fuels. The stoichiometric ratios were set so that the amount of elements on the left side of the equation (reactants) matched up with the right side (products). Nitrogen was added as a product and a reactant, even though it didn't end up managing to make a big difference. Ethanol seemed to have the lowest heating value, at 27.668 MJ/kg, Butyl-Acetate with 28.652 MJ/kg, and finally 2-Methylfuran with the highest LHV with 31.790 MJ/kg. So far, Butyl-Acetate seems to be the best contender in terms of replacing ethanol within gasoline simply because of its lower heating value than that of 2-methylfuran, and its lower energy usage throughout the production process with a high potential of having a crazy

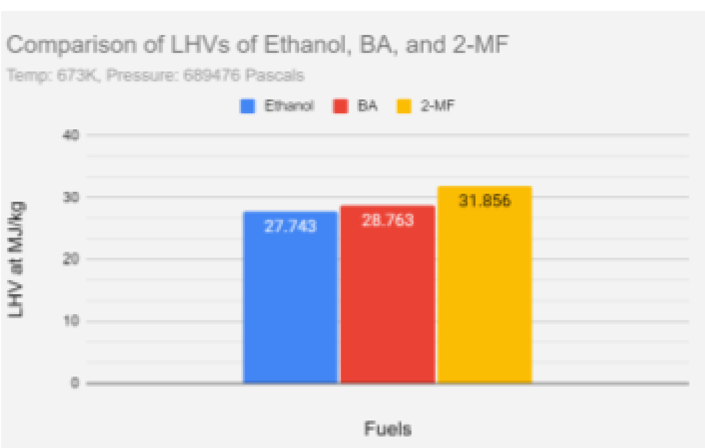

Fig 1. This chart compares the base LHVs of the considered alternative fuels, visually enhancing which fuels are more efficient energywise during combustion

high enthalpy amount. There is no point alternating temperatures and pressures to generate different data, the point being, ethanol is more thermodynamically efficient than BA and 2-MF when it comes to the amount of energy lost as heat per kg of fuel used.

Pre-ignition data is something else that will help determine whether or not 2-MF and BA could replace Ethanol within the gasoline mixture. This is because the better the pre-ignition time, the better the rate of combustion within the gasoline engine, and the lower the amount of energy being wasted. This is simply because of higher efficiency resulting in a lower amount of energy used. If the ignition delay times of alternative biofuels are better than that of ethanol, the biofuels could have a real possibility of replacing ethanol. The limitation with better ignition delay times however, is that if the ignition delay time is too little, there is an increased chance of problems such as rod knocking happening. Using the Cantera example code provided within the examples section, and swapping out the mechanism for something that is a combination of both the MIT-ButylAcetate mechanism and the 2-Methylfuran mechanism from Creck Dynamics Explosion lab, we can determine that the pre-ignition time of Ethanol is that of .01856 seconds without adjusting the temperature or the pressure. Adjusting the temperature and pressure to that of an actual engine, .0292 seconds was the answer. Keep in mind this is only regarding pure Ethanol, this doesn't include a substantial amount of gasoline. As for BA and 2-MF, their values are .015 seconds and .05 seconds respectively. Again, these fuels have been calculated with pure biofuels themselves, no gasoline or ethanol was added to alter the data. So far looking at the pre-ignition data, BA tends to have a lower ignition delay time than that of ethanol, meaning it is wasting less energy every time the engine does a combustion process.

Data generation for blends poses a few issues which were soon resolved. The use of 2 different mechanisms were needed to be used at the same time in order to compute data including BA and gasoline simply because gasoline wasn't included as a fuel within the BA mechanism. Another problem posed by the data generation is that of gasoline. Raw gasoline is made up of many different chemicals, so much so that DOE refers to gasoline's chemical structure as C4-C16 [4]. Therefore a gasoline surrogate had to be used, a surrogate being having similar properties of that of gasoline while not being nearly as complicated. Not only did this save time during data analysis, it made the process a whole lot simpler. The surrogate would consist of 84 octane and 16 heptane, because it had the properties most similar to that of gasoline [21]. To keep everything simpler, the O2 amount was either set to 10 or 11. A slightly modified version of the example code was used as well, a type of reactor was enforced to make sure that the volume is the same throughout the ignition delay times. Some of the ignition delay data may look extreme, but this is because the amount of volume is kept consistent throughout the simulation, whereas the other example code may or may not have done this, along with the removal of Nitrogen to simplify the process even further. The point being, if through altered pressure, the ignition delay time is similar through that of a gasoline surrogate and their co-respective blends, the performance will

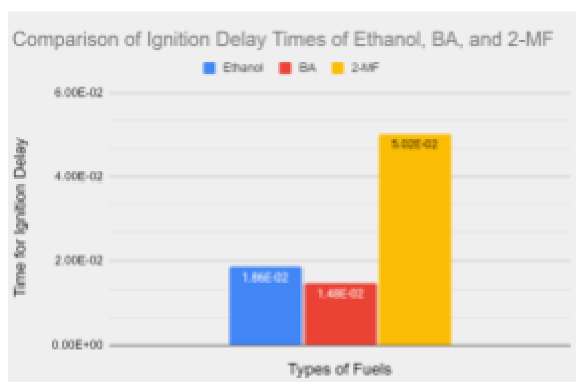

Fig 2. This chart highlights the ignition delay times of that of 2-MF, BA, and Ethanol, showcasing that BA has a lower ignition delay time of that of ethanol and 2-MF

be very similar within the fuels. The gasoline surrogate on its own represents the highest quality of octane that is available at the pump, whereas the gasoline surrogate + ethanol blend represents the cheapest type of gas available at the gas station.

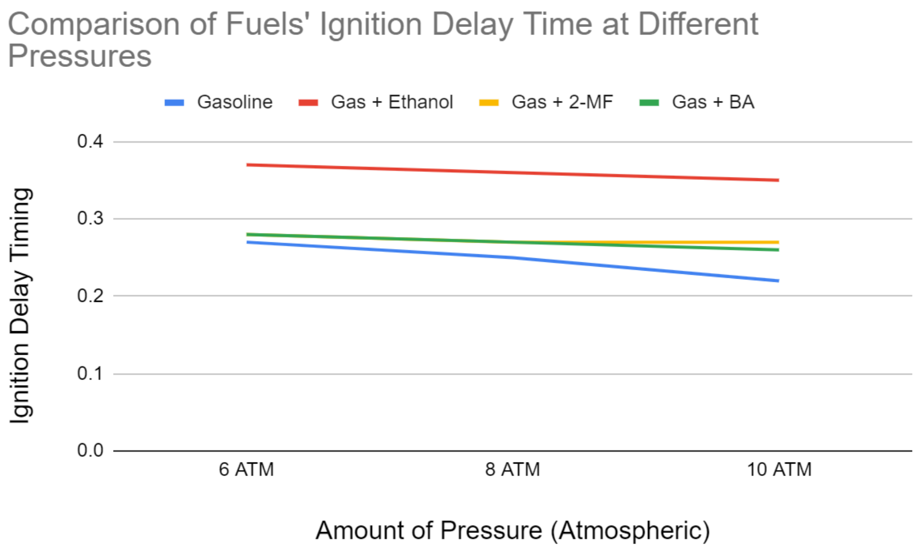

Fig 3. This graph displays the ignition delay timing throughout the simulation process, most notably highlighting that gasoline has the best ignition delay timing, followed by gas + BA, gas + 2-MF, and gas + ethanol.

4. Discussion

Even with data generation, fuel properties are another factor in whether or not the replacement of ethanol could happen. This is because ethanol and gasoline have been implemented as "gas" in cars in 2001 and newer [16]. A blend of 10-15% ethanol and 85-90% gasoline have been standardized in cars. Gasoline engines are heavily optimized to run on fuel properties, and the goal of this article is to make sure that the replacement of ethanol takes place without needing engine modifications.

To start, there has to be a baseline of what the fuel properties of the gasoline, ethanol blend "gas" is. The density of a gas is 0.722g/mL. If the density were to exceed that amount by greater than a factor of 0.1, there would be major complications within the engine system. This is a reason why E100 doesn't work well within regular cars, despite having a density of 0.79g/mL [20]. This is because even a slight change in density can cause issues within the systems of the engine such as the valves, fuel lines, and the cylinders, often leading to problems such as stalling or incomplete combustion. This reason is similar to why diesel doesn't work within gasoline engines, because the fuel is too thick to properly run. Another fuel property that has been optimized to run in gasoline engines is that of the flash point. Although this property may not play a huge impact because the spark from the spark plug is around 500 to 800 C [22], so as long as there is a relatively low flash point, this should not be an issue for the combustion engine to deal with. The last fuel property that may affect whether or not 2-MF or BA can replace ethanol with gasoline is that of solubility. Solubility within ethanol is not important when looking at whether or not these fuels can replace ethanol. But if these fuels are soluble in ethanol, then there could be a possibility of a 3 way blend within gasoline, ethanol, and an additional biofuel.

As for the properties of the blends themselves, BA and 2-MF have relatively low percentages when mixed with gasoline to produce the same density. Only 7% of BA can be added to match the density of the 15% ethanol blend, and only 5% of 2-methylfuran can be added to match the same density. This means that these fuels have to have 2 to 3 times better ignition delay time to match the amount of energy that the 15% ethanol blend uses. There is a higher amount of gasoline being used with the blends than with the new biofuels. The higher amount of gasoline causes problems because of the total amount of energy being used. These values were taken into consideration while data generation happened. Although it is pretty clear that fuels such as BA and 2-MF overpower ethanol regarding production to combustion because of an extremely high amount of enthalpy required to match the energy per gallon of ethanol, the overall energy used throughout combustion substantially increases because of the increased amounts of gasoline used within these blends. Other fuel properties such as the ability to blend with ethanol, only 2-Methylfuran can do so, BA is not soluble with ethanol, which causes further problems within the system because insolubility means separation during combustion.

If the overall goal were to cut off the most amount of gasoline possible through the use of a possible 3 way blend, reducing strain on ethanol and implementing possible alternatives could be the solution. The only realistic problem with using a 3 way solution would be the thickness factor. The density of E15 is around 0.722g/mL as previously mentioned various times within this study. The limitation of reaching this density would cause issues as only 5% 2-MF can be used before reaching this potential density limit. Therefore a possible 3 way solution could exist, but it would end up increasing the ratio of gasoline because of the high densities of these alternative fuels.

4.1 Data Analysis

Throughout the investigation of the production processes and the combustion processes, it is true that these biofuels are more thermodynamically efficient in all aspects, because of the experimental machinery being extremely efficient, and the potential for extremely high amounts of enthalpy, particularly within BA. It becomes evidently clear that these biofuels have an ignition delay time very similar to that of gasoline throughout the data generations. This could be explained by the higher ratio of gasoline being implemented due to the problems regarding density of these fuels, but also because these raw fuels tend to have better ignition delay times of that of ethanol, with the exception of 2-MF. While the data does suggest that LHVs for these biofuels are higher than that of ethanol, the efficiency of the production process does negate the increased LHV. Biofuels such as BA and 2-MF are more thermodynamically efficient from production to combustion, their application in the real world isn’t realistic because of the increased amount of gasoline required while these fuels are going to be used. A possible solution to this problem is to use flex fuel vehicles instead of regular vehicles. But another problem with that solution is that the majority of the cars within the US are purely gasoline cars, 20 million compared to 200 million [1], meaning that solution is redundant.

5. Conclusion

Investigation of the possibility of novel biofuels being able to replace ethanol in the real world was conducted. The main focus was to figure out whether or not biofuels once highlighted in DOE's Co-Optima Program would be able to thermodynamically be more efficient than that of ethanol through production to combustion. Although results find that these novel biofuels, primarily BA, tend to have more energy savings through production because of a potential of extremely high enthalpy amounts, and similar LHVs of that of ethanol, more gasoline is going to be needed within blends consisting of BA as compared to ethanol. A maximum of 15% ethanol can be added to gasoline before the density of the fuel requires modifications to internal combustion engines, whereas only 7% of BA and 5% of 2-MF can be added to gasoline to regulate the same density of that of 15% ethanol). These fuels cannot replace ethanol due to the increased amounts of gasoline offsetting the energy saved through the production of these biofuels, there is a possibility of a 3-way blend that may prove to be more efficient than the current solution of 15-85 ethanol-gasoline mix. Future research should further investigate the possibilities of other novel biofuels replacing ethanol, and understand the 3-way blend which would be most efficient to run in gasoline engines without significant/if any modifications.

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