Spray Characterization and Combustion Processes in a Constant Volume Chamber of Acetone-Butanol-Ethanol (ABE)

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Abstract

Butanol, in comparison with ethanol, has more similar properties of current transportation fuel. These means it has a potential of being a more suitable blend for use in diesel engines. Unfortunately, butanol has a high cost of production. Acetone-butanol-ethanol (ABE) is an intermediate product of the fermentation process of butanol production. By using ABE directly in diesel fuels instead of butanol, the separation and purification processes are eliminated. As a result, it has a potential for greatly decreasing the overall cost for fuel production. This could lead to a larger commercial use of ABE-diesel blends on the market. Research has been conducted over the past five years regarding spray and combustion processes of both neat ABE and ABE-diesel blends. The main focus of this paper is to review the efforts made in fundamental spray research under quasi-steady flow field environments provided by a high-temperature, high-pressure constant volume chamber. Heat release rates high-speed Mie-scattering images were acquired from in-cylinder pressure traces to characterize liquid spray penetration. Natural flame luminosity was also captured to depict spatial and temporal soot distribution. It is observed that the acetone content has a major influence in the combustion behavior of the ABE mixture. As the acetone content increases, the combustion phasing significantly advances. Butanol is able to compensate the advancing effect caused by acetone and ethanol. Additionally, butanol can increase the overall energy density of the mixture and as a result makes the properties of the mixture closer to that of diesel.

Key words: ABE, Acetone, Butanol, Ethanol, Diesel, Constant-Volume Chamber

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Introduction

Bio-fuels, i.e. fuels derived from agricultural sources, offer the exciting possibility of “renewability” in the sense that the plants that produce the fuels can be regenerated by the eco-system using the combustion products of the fuels. In this manner, power generation can be achieved with significantly reducing its contribution to climate change. So far, research in this area has developed along two completely independent lines with the dominant trend being the production of pure chemicals from agricultural processes. On one hand, a significant amount of work has focused on the “upstream”: biological processes that produce these pure fuels in an efficient and environmentally friendly way from appropriate raw materials. On the other hand, the study of “downstream”, chemical and mechanical processes that relate to application of bio-fuels to the transportation and power generation sectors, are rapidly developing.

Bio-fuels are of particular interest to the automobile industry and other areas in energy and environment because they have the potential of significantly reducing particulate (PM), hydrocarbon (HC) and CO emissions under certain load conditions [1]. In addition to their benefits of regulating exhaust emissions, bio-fuels contribute less to climate change than fossil fuels due to their closed carbon cycle. There is almost no net increase of CO2 emissions from bio-fuel combustion as the plants, from which biofuels are derived, absorb CO2 from the atmosphere. Moreover, bio-fuels are particularly attractive because they are renewable fuels that can be replenished through the growth of plants. Additionally, they have the potential to supply a significant fraction of petroleum-based fuels.

At present, ethanol and biodiesel are the forerunners in the adoption and commercialization of biofuels. Since the late 1970’s, Brazil has had a program to replace gasoline with ethanol in motor vehicles [2]. Ethanol-diesel blends have also received attention over the same period of time. However, technical and safety issues still need to be solved before such blends can move to the commercialization stage [3, 4]. Biodiesel production is rapidly expanding globally and extensive testing of biodiesel from various sources has verified the potential for this fuel to be successfully used in diesel engines [5, 6]. While ethanol and biodiesel are the major focus for biofuels at the present time, there are other biomass-derived fuels that exhibit properties which make them potentially more attractive.

This paper gives a comprehensive review of the methods used for producing ABE mixtures, several experimental investigations on the spray and combustion processes of ABE and ABE-diesel blends. In the end, the authors provide a brief summary for the merits and challenges for the application of ABE.

Production of ABE Mixtures

A recently emerging bio-fuel is butanol, which was recently produced through an anaerobic process involving a fermentation microorganism. Renewable biomass resources such as whey permeate, corn, wood hydrolysate, starch and other monomer sugars can be used to produce butanol. [7-9] During the fermentation process in which a 3:6:1 acetone: butanol: ethanol mixture, referred to as baelene, is obtained [8, 10]. ABE fermentation has been of interest as an alternative method for generating these chemicals, rather than relying on petrochemicals for their production. This interest has been recently accentuated by the high cost of petrochemicals and the drive towards less dependence on petroleum. At present the genome sequence for the microorganisms that produce the solvents is being determined and, once available, will allow investigators to unravel the general principles of solvent production. This will ultimately lead to a rational metabolic engineering-based approach for the development of second-generation strains with characteristics that are optimized for the production of biosolvents or bio-fuels from renewable sources.

Acquiring the pure butanol from the fermentation solvent is based on the combination of acetone-butanol-ethanol distillation. [9] The cost of recovering butanol through distillation is high because its boiling point of 118°C leads to a high-energy input in the distillation process (bio-butanol contains mainly 1-butanol and small quantities of the other isomers that have different boiling points). Being able to make use of the ABE mixture as a bio-fuel, referred to as baelene, without having to execute a further distillation step will lead to substantial cost and energy savings. Several important characteristics of the combustion process in the engine cylinder (heat release, main combustion products) exhibit very little sensitivity to precise molecular structure of the fuel. [13] For this reason, it should be possible to operate engines in a clean and efficient manner using intermediate products of the fermentation process (like baelene) without the need to produce pure chemicals (like butanol or ethanol). However, the possibility of operating with a fuel blend raises the question of blend composition optimization, i.e. “guiding” the baelene production process towards the proportion of butanol/ acetone/ ethanol that will be optimal in terms of both cost-efficient production and clean and efficient performance.

Characterization of ABE Fuel Properties

The chemical and physical properties of the species concerned with this research are tabulated. Also, some basic mixture properties of the blended fuel concerned in this paper are calculated, as shown in Table 1.

A simple conclusion can be made from the table: all single components of the ABE mixture show higher auto-ignition temperature, lower LHV, lower boiling
point and a higher latent heat. The addition of the ABE mixture into diesel will improve the volatility of the mixture, while also a retarded auto-ignition can be expected due to both the limitation of the auto-ignition temperature and the effect of vaporization cooling.

**Experiments**

There have been quite a lot of works on the performances and emissions of alcohol-gasoline or alcohol-diesel mixtures in engine tests. Some general conclusions include these observations are given: when blending ABE with gasoline in a low percentage (up to 40%), the overall combustion characteristics are similar with pure gasoline, meaning a good interchangeability of ABE with use in SI engines [18]; when blending with gasoline or diesel, a noticeable reduction in particulate matter (PM) and polycyclic aromatic hydrocarbons (PAH) can be observed, due to the oxygen-content nature of ABE [19]. However, NOx emissions are different, since the volatility of alcohols is higher than that of diesel. A better fuel-air mixture process can be expected, which further leads to a more premixed-dominant combustion. NOx formation will be favored under this condition due to an elevated combustion temperature [19, 20]. Some research results indicate that this increment in NOx can be suppressed by certain amount of EGR or by a small quantity (0.5~1.0%) of water addition in the ABE blend [19].

Despite of the abundant discoveries that have been made in engines, the combustion process inside a real engine cylinder is quite complex and it is an overall behavior controlled by multiple factors that are highly coupled together. In order to investigate the fundamental nature of the spray at engine-like conditions, constant volume chambers are used to isolate those factors and focus on the thermodynamic process at a quasi-static flow field. In this article, recent works of ABE spray combustion in constant volume chambers will be the main focus.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Diesel</th>
<th>Acetone</th>
<th>Butanol</th>
<th>Ethanol</th>
<th>ABE20 (6:3:1)</th>
<th>ABE20 (3:6:1)</th>
<th>ABE20 (0:10:0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₁₂₋C₂₅</td>
<td>C₃H₆O</td>
<td>C₄H₉OH</td>
<td>C₂H₅OH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetane number</td>
<td>&gt;40</td>
<td>25</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen content (wt %)</td>
<td>0.82-0.86</td>
<td>27.59</td>
<td>21.62</td>
<td>34.78</td>
<td>5.08</td>
<td>4.77</td>
<td>4.21</td>
</tr>
<tr>
<td>Density at 288 K (g/mL)</td>
<td>0.791</td>
<td>0.813</td>
<td>0.795</td>
<td>0.832</td>
<td>0.833</td>
<td>0.833</td>
<td>0.835</td>
</tr>
<tr>
<td>Auto-ignition temperature (K)</td>
<td>503</td>
<td>833</td>
<td>658</td>
<td>707</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower heating value (MJ/kg)</td>
<td>42.7</td>
<td>29.6</td>
<td>33.1</td>
<td>26.8</td>
<td>40.34</td>
<td>40.53</td>
<td>40.83</td>
</tr>
<tr>
<td>Boiling point (K)</td>
<td>555-561</td>
<td>329.2</td>
<td>390.8</td>
<td>351.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Latent heat at 298 K (kJ/kg)</td>
<td>270</td>
<td>518</td>
<td>582</td>
<td>904</td>
<td>328.7</td>
<td>332.8</td>
<td>330.8</td>
</tr>
<tr>
<td>Flammability limits (vol. %)</td>
<td>0.6-5.6</td>
<td>2.6-12.8</td>
<td>1.4-11.2</td>
<td>4.3-19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturation pressure at 311 K (kPa)</td>
<td>0.3</td>
<td>53.4</td>
<td>2.27</td>
<td>13.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity at 413 K (mm²/s)</td>
<td>1.9-4.1</td>
<td>0.35</td>
<td>2.63</td>
<td>1.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laminar Flame Speed (cm/s)</td>
<td>~34ᵃ</td>
<td>~48ᵇ</td>
<td>~39ᶜ</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: (1) Properties of diesel are from ASTM D975, properties of acetone are from [14, 15], properties of ethanol and butanol are from [14-16]. (2) Laminar flame speed data from [17], under conditions: a- 1atm, 298K; b- 1atm, 343K, c- 1atm, 325K.

**Table 1.** Physical and thermodynamic properties of ABE-diesel blends and their pure components.
Most of the experiments in the reviewed articles were conducted in a pre-burn type constant volume chamber, which is capable of providing high-temperature and high-pressure conditions identical to the conditions upon injection in a real metal diesel engine. Figure 1 shows a typical structure of a pre-burn type constant volume chamber. A fused silica quartz window was mounted at the top of chamber to provide optical access. The chamber wall was heated to prevent water condensation on either chamber walls or windows. Detailed introductions to the typical experimental setup can be found in Ref. [21].

Optical diagnostic techniques were applied in the experiments to capture the liquid phase spray image and also the soot distribution during combustion. Pressure traces were captured using a KISTLER pressure transducer and apparent heat release rate (AHRR) was derived. Apart from AHRR, various quantitative indicators were automatically processed by computerized codes from images to further analyze the processes. Detailed description of data processing methods can be found in Refs. [21,22,23].

Impact of Butanol Contents

There is quite a lot of work done recently on the combustion characteristics of both neat butanol and butanol-diesel blends, mainly because butanol is similar to the current transportation fuels in some thermodynamic properties, such as longer hydrocarbon chain, higher energy density and higher cetane number.

Butanol has four different forms of isomer: n-butanol, sec-butanol, iso-butanol and tert-butanol. Although they share the same formula, due to different structures of these isomers, the physical properties (boiling point, density, viscosity, etc.) are quite distinct. Wu and Law [25] further discovered that the isomers also have quite different laminar flame speed and Markstein length, with n-butanol shows the maximum laminar flame speed. Through reaction path analysis, the authors identified that the other three isomers will be turned into some intermediate species which are more stable and are of low reactivity. Liu et al. [21,26] investigated the spray liquid penetration length, combustion heat release rate and soot emission characteristics of pure n-butanol in comparison with biodiesel. Compared to biodiesel, n-butanol exhibits a higher normalized peak combustion pressure, which is a result of larger quantity of heat released in a shorter time period, indicating higher combustion efficiency in constant volume combustion, due to the higher energy conversion efficiency and lower heat loss. In accordance, the natural flame luminosity of n-butanol is lower than that of diesel, meaning a more complete combustion. Liu and Li [27-29] investigated how n-butanol affected diesel and biodiesel mixtures. These n-butanol, diesel, and bio-diesel blends were tested inside a constant volume chamber to investigate the liquid spray and combustion of the fuels. The authors found that when the ambient temperature was higher, the spray jet penetration was shortened due to a faster liquid evaporation. Additionally, with more n-butanol added to the mixture, the spray penetration length was also reduced. Furthermore, microexplosions, which are caused by internal gasification of a liquid mixture with different volatilities and boiling points, increased with the increase of n-butanol. This is due to the higher volatility of the n-butanol in comparison to the diesel and biodiesel. The microexplosions in turn also reduce spray penetration. Liu also discovered that with the addition of more n-butanol, the spray jet angle of the fuel blend increased. This is because after adding the n-butanol, the viscosity and surface tension are reduced. On the other hand, the diffusion rate and the air entrainment of the spray were both enhanced. As a result, the droplet has an easier time atomizing into uniform droplets. In other words, adding appropriate amounts of n-butanol to a biodiesel blend can acquire similar spray characteristics as diesel. This in turn can effectively reduce hydrocarbon and particulate emissions.

In terms of combustion characteristics, Figure 3 shows the pressure trace and apparent heat release rate of tested fuels under different temperature conditions. At higher temperature, ABE100 and B100 show similar combustion phasing and AHRR shape. However as the ambient temperature decreases, the deviation between these two fuels starts to become evident, as ABE100 generally showed retarded combustion phasing and even lower peak AHRR than B100. This characteristic is similar with the observation in liquid penetration lengths, because the evaporation process is a major factor that controls the initial stage heat release pattern: with a shorter penetration length, better liquid fuel at-

Figure 1. Inner structure of a pre-burn type CVC, experiment setup as shown in Ref. [21].
omization and evaporation can be expected and thus leading to a more rapid pressure rise, in this way, spray penetration length can be correlated to the heat release rate, which is consistent with the observation in this research.

The proximity of modifying the ABE mixture in both evaporation and combustion ABE100 and n-B100 characteristics in terms of both spray and combustion also revealed that butanol as the most redundant species in ABE mixture, has the effect of controlling overall spray and combustion characteristics. In the application of ABE fuel, certain amount of butanol in ABE mixtures are desired for the following purposes: (1) Increase energy density of the mixture; (2) Adjust the overall volatility of mixture to an appropriate level; (3) Counteract the retardation effect of acetone and ethanol to an appropriate level.

Apart from these merits, as observed by Wu [30], higher butanol content may cause an increment in soot emission. Figure 4 shows the spatial integrated natural flame luminosity (SINL) of pure diesel, ABE and n-butanol during constant volume combustion, which adds up pixel-by-pixel natural flame luminosity to evaluate the overall luminosity emission during combustion. The natural luminosity results from two sources: chemiluminescence and soot incandescence. However, in general combustion cases, the intensity of soot incandescence, which depends on local soot concentration and soot particle temperature [24], is much stronger than the former one [31]. In this way, it can be expected that SINL is an indicator for overall combustion cleanliness. As is shown in Figure 4, The SINL curve of B100 has a higher peak than that of ABE100. However, the reduction in soot concentration of both ABE100 and B100 compared to pure diesel is already quite satisfactory.

Impact of ABE-Diesel Blending Ratios

As a convention in the market, biofuels or alcohols are usually blended with commercial transportation fuels at a certain ratio. In order to study the impact of ABE-diesel blending ratios, researchers in author’s group have done a lot of work via both experimental and simulation approach. In this part, several works on spray and combustion characteristics of different ABE-diesel blends will be summarized.

Zhou et al. [32] investigated ABE-diesel blends at a volumetric ratio of 50% (referred to as ABE50) and 80% (referred to as ABE80, ratio in terms of ABE) at low temperature conditions. Later, Zhou et al. [33] performed similar experiments for ABE-diesel blends at a volumetric ratio of 20% (referred to as ABE20). Wu et al. [34] analyzed combustion characteristics of ABE20 at various temperature and ambient oxygen concentration conditions. Lin et al. [23] further focused on a high-percentage ABE-diesel blend (ABE80). Here in this part, data from all these papers are gathered to offer a better representation of blending ratio influences.

![Figure 2. Liquid penetration length of pure diesel, ABE and pure butanol at different ambient temperature conditions [30].](image)

In terms of liquid penetration length, no figures will be shown in this paper, because the conclusions are obvious and predictable: with the addition of ABE in diesel, a shortened liquid penetration length will be observed. Also, similar to previous results, as the ambient temperature decreases, the deviation between fuels will start to stand out more obviously, owing to the difference in volatility of ABE and diesel.

In terms of combustion characteristics, Figure 5 shows the combustion pressure and AHRR curves for the tested fuels. Note that the lines are not spreading with the same sequence of increased ABE content: ABE50, although contains more ABE, appear to be more advanced in the combustion phasing than ABE20. This observation indicates that there are at least two competing factors that are influencing combustion characteristics at the same time. Some obvious factors include the low cetane number and the high latent heat value of ABE, which will both lead to a retarded auto-ignition timing. Other reasons that will lead to ad-
Advanced combustion timing could be a better fuel-air mixing prior to combustion, as the high oxygen content improves the local air-fuel ratio. Due to this competing process, ABE20 suffers from higher latent heat and lower cetane number resulted by ABE. But this is not compensated through enhanced evaporation and fuel-air mixing, which leads to an overall retarded combustion phasing. ABE50 seems to be the best ratio among the tested fuels, for its proximity in combustion characteristics with diesel and thus providing a potential to be directly used in an engine without the need of modification. It can also be inferred that there should be an optimal ABE-diesel blending ratio, to better balance these competing factors.

In terms of soot emission during combustion, SINL evolution histories of tested fuels under different ambient oxygen concentrations and ambient temperature conditions are presented in Figure 6. Some general conclusions concerning low soot emissions during low temperatures and low ambient oxygen concentrations can be easily made, indicating that LTC and EGR are still effective soot controlling strategies of the ABE-diesel mixture combustion.

**Figure 3.** Combustion pressure trace and apparent heat release rate of pure diesel, ABE and pure butanol at different ambient temperature conditions [30].

**Figure 4.** Spatial integrated natural flame luminosity of pure diesel, ABE and pure butanol at 1200K ambient temperature condition [30].

**Figure 5.** Combustion pressure and apparent heat release rate of ABE20, ABE50 and ABE80 [35].

A proportional relation between ABE concentrations in diesel blend and maximum SINL value can be observed under all conditions. Also, note that the width...
of SINL plateau is decreased with the increased ABE ratio. These findings are both attributed to the oxygen content in ABE mixtures. On one hand, oxygen content will improve the local equivalence ratio during the non-premixed combustion process, which can significantly decrease the generation of soot precursors. On another hand, the overall lean-mixture due to the oxygen content in fuels will accelerate the soot oxidation process, resulting in a shortened soot presence time.

Conclusion

This paper summarized the recent works focused on the issues concerning a new biofuel: acetone-butanol-ethanol (ABE) when blended with diesel, while focusing on a more fundamental approach to investigate the spray and combustion process in a quasi-static flow conditions. Some main conclusions include:

- Butanol has a minor effect on ignition delay time, but it is a crucial component for the ABE mixture, acting as a “mediating” species to compensate the degree of combustion phasing advancement caused by acetone and ethanol. Also, butanol has the highest heating value, which is important for the increase of overall fuel energy density.
- Blending the ABE mixture with diesel has a proportional effect of decreasing soot emission and accelerating soot oxidation. However, the combustion characteristic of the ABE-diesel mixture is dominant by several competing factors. An optimal ratio of ABE in diesel exists near 50% which will produce a similar behavior as pure diesel.

Based on the review, several undermined yet important topics of ABE research is needed:

- Validate the effect of ethanol in ABE-diesel mixtures, in terms of both combustion characteristics and pollutant emissions.
- Construct guidelines for optimizing ABE-diesel blending ratios, including the identification of competing factors and numerically modelling of optimization problems.
- Validate the results using experimental results of ABE-diesel fuelled diesel engines.

However, several challenges are faced in this area of research, which need to be considered for the future work.

- Due to the composition of ABE mixture, single-factorial design of experiment is not possible: changing concentration of one component will surely affect the other two. This issue makes the conclusions unconvincing, and obstructs the quantitative analysis of the problem.
- Incomplete reaction during premixed combustion of constant volume chamber can be expected. However, the minor species during this incomplete combustion process could act as precursors or introduce radicals for the following spray combustion process. Analysis of the degree of reaction and species after premixed combustion is important.

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![Figure 6. Spatial integrated natural flame luminosity of ABE20, ABE50, ABE100 and pure diesel in various temperature and ambient oxygen concentration conditions.](image-url)