

A Semi-Detailed Chemical Kinetic Mechanism of Acetone-Butanol-Ethanol (ABE) and Diesel Blends for Combustion Simulations

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ABSTRACT

With the development of advanced ABE fermentation technology, the volumetric percentage of acetone, butanol and ethanol in the bio-solvents can be precisely controlled. To seek for an optimized volumetric ratio for ABE-diesel blends, the previous work in our team has experimentally investigated and analyzed the combustion features of ABE-diesel blends with different volumetric ratio (A: B: E: 6:3:1; 3:6:1; 0:10:0, vol. %) in a constant volume chamber. It was found that an increased amount of acetone would lead to a significant advancement of combustion phasing whereas butanol would compensate the advancing effect. Both spray dynamic and chemistry reaction dynamic are of great importance in explaining the unique combustion characteristic of ABE-diesel blend.

In this study, a semi-detailed chemical mechanism is constructed and used to model ABE-diesel spray combustion in a constant volume chamber. This mechanism comprises Acetone, Butanol, Ethanol and n-heptane as surrogate fuel species. Validations are conducted for the present mechanism with results from literatures. KIVA-3V program coupled with the validated mechanism is used to simulate the spray dynamics and combustion characteristics inside the constant volume chamber. Simulation results and previous experimental data are presented and discussed in detail. Reasonable agreements both in shock tube simulation and constant volume chamber simulation of ignition delay, cylinder pressures and heat release rates were achieved between experimental and calculated results. In summary, the presented semi-detailed chemical mechanism is demonstrated to be computational acceptable in timescales while maintaining the kinetic behavior of newly studied ABE-diesel blends.

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INTRODUCTION

In recent years, alcohols, such as ethanol and butanol, have received extensive attention as promising alternative fuels due to increasing environment awareness and depleting fossil fuel resources[1,2]. Numerous studies have shown that using alcohols as additives to conventional diesel fuel can considerably reduce the amount of carbon monoxide (CO), total hydrocarbons (THCs) and particulate matter (PM) in the exhaust, with additional potential benefits on NOx emissions since the extra oxygen content in alcohols enhances the oxidation of soot, CO and THC[3,4,5,6].

While ethanol has been the primary commercially used fuel additive, particularly as a blending agent with gasoline in SI engines, recent research has been shifting towards the study of longer-chain alcohols such as butanol[7,8]. Butanol features numerous advantages over the short-chain alcohols when used as a blending component in petroleum diesel fuels, including higher energy density and cetane number, greater miscibility in conventional diesel fuel, lower vapor pressure and heat of vaporization, and more immunity to the effects of water contamination[9,10]. These features endorse butanol the compatibility with existing fuel distribution infrastructure.

butanol-diesel blends can work as a drop-in replacement in most internal combustion engine (ICE) without major engine or fuel system modifications[11,12].

Acetone-Butanol-Ethanol (ABE) fermentation, as one of the major butanol bioproduction methods, produces Acetone, Butanol and Ethanol mixture in a ratio of 3:6:1. The key problems associated this method are the cost of substrate and butanol toxicity/inhibition of the fermenting microorganisms, resulting in a low butanol titer in the fermentation broth[13,14,15]. If directly blending Acetone-Butanol-Ethanol mixture with commercial diesel fuel, the separation and purification processes which are necessary for butanol production could be dispensed. As such, ABE biofuel has the potential of greatly decreasing the overall cost for fuel production and increasing chemical yield of biofuel if directly used in diesel blends[16]. Simultaneous reductions in PM and NO_x emission are observed in Recent studies on the combustion of ABE-diesel blends in diesel engines[17]. Optical studies on combustion characteristics of neat ABE and ABE-diesel blends in a combustion chamber were carried out to find that ABE provides tremendous soot and NO_x reduction capabilities[18,19,20]. The performance and emission investigation of ABE-gasoline blends on SI engine showed that a small amount of ABE addition resulted in an efficiency enhancement [21,22,23,24]. Moreover, Water containing ABE-gasoline blends was demonstrated to be more effective in inhibiting NO_x and CO emission, but showed elevated unburned hydrocarbon (UHC) [25].

Meanwhile, an optimal ratio of ABE-diesel blends is applicable in recent years since the recent ABE fermentation technology is capable in precisely controlling the volumetric ratio of the three components in broth. To explore the optimal ABE ratio, Wu et al.[2,25] carried out preliminary experimental studies on the combustion characteristics of ABE-diesel blends with different volumetric ratios of acetone,

butanol and ethanol using a constant volume chamber under an ambient temperature of 800 K with 3 different ambient oxygen concentrations. They concluded that the ignition delay decreased and the combustion duration shortened with the increase of acetone and the addition of acetone is very effective in suppressing soot emission. Lee et al.[26] reviewed these experiments and concluded that acetone agent advances combustion phasing whereas butanol content compensates the advancing effect caused by acetone. They also commented that both spray dynamic and chemistry reaction dynamic are of great importance in explaining the unique combustion characteristic of ABE-diesel blends.

However, despite the emerging experimental interests on combustion characteristic ABE-petroleum fuel blends, fundamental numerical methods and the chemical kinetic mechanisms for ABE mixtures have remained largely unstudied, let alone those of ABE-petroleum fuel blends. Zhao et al.[27] developed a multi-step ABE phenomenological soot model and implemented it into KIVA-3V Release 2 code. However, this phenomenological model needs further validations under a wider range of operation condition to justify its predictivity. Van Geem et al.[28] developed a detailed combustion and pyrolysis mechanism of ABE mixtures. Their model shows a relevant deviation of butanol at ~ 30% butanol conversion. The sensitivity study of their model indicates the direct molecular dehydrogenation reaction of butanol further contributes to butanol formation.

Therefore, the primary motivation of this study is to construct a fundamental mechanism for the combustion ABE-diesel blends and implement it to CFD code KIVA-3V Release 2 to model the spray combustion of ABE-Diesel blends with different component volumetric ratio, (A: B: E: 6:3:1; 3:6:1; 0:10:0, vol. %), in a

Table 1. Physical and thermodynamic properties of ABE-diesel blends and their pure components.

Properties	Diesel	Acetone	Butanol	Ethanol	ABE20 (6:3:1)	ABE20 (3:6:1)	ABE20 (0:10:0)
Molecular formula	C ₁₂ -C ₂₅	C ₃ H ₆ O	C ₄ H ₉ OH	C ₂ H ₅ OH			
Cetane number	>40		25	8			
Oxygen content (wt %)		27.59	21.62	34.78	5.08	4.77	4.21
Density at 288 K (g/mL)	0.82-0.86	0.791	0.813	0.795	0.832	0.833	0.835
Auto-ignition temperature (K)	503	833	658	707			
Lower heating value (MJ/kg)	42.7	29.6	33.1	26.8	40.34	40.53	40.83
Boiling point (K)	555-561	329.2	390.8	351.5			
Stoichiometric ratio	14.3	9.54	11.21	9.02	13.47	13.57	13.7
Latent heat at 298 K (kJ/kg)	270	518	582	904	328.7	332.8	330.8
Flammability limits (vol. %)	0.6-5.6	2.6-12.8	1.4-11.2	4.3-19			
Saturation pressure at 311 K (kPa)	0.3	53.4	2.27	13.8			
Viscosity at 413 K (mm ² /s)	1.9-4.1	0.35	2.63	1.08			
Laminar Flame Speed (cm/s)		~34a	~48b	~39c			

constant volume chamber under low temperature 800K. This mechanism has been validated against single component experimental ignition delay times extracted from literatures. In addition, the unique combustion characteristic of ABE-Diesel blends is preliminarily discussed from chemical mechanism perspective. Table1 displays the physical and thermodynamic properties of ABE-diesel blends and their pure components.

BASE MECHANISMS

Considering that ABE-diesel blends mainly consist of acetone, butanol, ethanol and diesel contents, its surrogate fuel model components must also reflect chemical structures of all these contents. As such, the proposed mechanism comprises Acetone, Butanol, Ethanol and n-heptane as surrogate fuel species.

An understanding of acetone oxidation kinetics plays an important role in combustion modeling of ABE-diesel blends. However, the previous work in this field is very limited. Hoare et al.[29,30,31] and Barnard and Hoyerman[32,33] studied the oxidation of acetone in gas-phase under low temperature(at <800K) several decades ago. Experiments of Oxidation and decomposition of acetone above 1000K in shock tubes were done by Tsuboi et al.[34] in the temperature range 1240-1620K and Sato and Hidaka[35] in the temperature range 1050-1650K, at pressures between 1.2 and 3.2atm and in the equivalence ratio range of 0.5-2. The recent work done by Chaos et al.[36] in a variable pressure reactor considered the oxidation and pyrolysis of acetone. Gibbs and Calcote[37] and Li et al.[38] also studied acetone as one part of their works in the flame experiments. Pichon et al.[39] investigated acetone oxidation in argon behind reflected shock waves in the temperature range 1340-1930K, at 1 atm and at equivalence ratios of 0.5, 1 and 2. Alzueta et al. [40] studied the oxidation of acetone both in the absence and the presence of NO under flow reactor conditions in the temperature range of 700-1500K.

Among all the butanol isomers, n-butanol is the predominant product through ABE fermentation and has been studied as a fuel or as a blending agent for use in spark-ignition engines[41], compression-ignition engines[42], and motored engines[43]. Several authors presented kinetic schemes of n-butanol based on previous work. Sarathy et al.[44] proposed a mechanism based on the jet-stirred reactor and laminar flame speed data. Moss et al.[45] created their mechanism based on the ignition delay measurements. The mechanism agreed well with their data but was only validated with high-temperature and relatively low pressure studies. Black et al.[46] studied the combustion properties of bio-butanol and presented a detailed chemical kinetic model of butanol isomers. Their mechanism was also only validated against high-temperature shock-tube studies. Grana et al.[47] extracted their mechanism from a semi-detailed C0-C16 mechanism from their previous work. Ignition delay results are validated against the high-temperature shock-tube studies from Moss et al.[45] and Black et al.[46]. Harper et al.[48] validated their mechanism across a wide temperature range, including the data of

Black et al.[46], Moss et al.[45], McEnally and Pfefferle[49] and Dagaut et al.[50], and their own pyrolysis experiment data. The ignition-delay results, however, have only been validated in the high-temperature regime.

Ethanol is at present the most widely produced and used biofuel as a neat fuel as well as an octane enhancer in gasoline. Hence, the investigations on its combustion chemical kinetics are more matured compared to that of acetone and butanol. Cancino et al.[51] measured ignition delays of ethanol with equivalence ratio of 0.3-1.0 after a shock tube at the temperatures in the range 770-1250 K and at pressures of 10-40 bar. Lee et al.[52] measured ignition delay for stoichiometric ethanol combustion at 775-1000 K and 80 bar using a shock tube. The original detailed chemical kinetic modeling work of Natarajan and Bhaskaran[53] investigated the ignition delay of ethanol over the temperature range 1300-1700K at pressures of 1.0 and 2.0 atm and equivalence ratios of 0.5, 1.0 and 2.0 in a shock tube. Dunphy and Simmie[54] base their mechanism on their measurements of ignition delay of ethanol-oxygen mixtures behind reflected shock waves from 1080 to 1660 K, in the pressure range 1.8-4.6 bar and with equivalence ratios varying from 0.25 to 2. Marinov[55] developed a detailed chemical kinetic model of the oxidation of ethanol in high temperature and validated it against extensive experimental data sets.

Commercial diesel fuel is a complex mixture of alkanes, aromatics, cycloalkanes, and olefins. It is not feasible to consider the oxidation chemistry of all the compounds. Thus, kinetic studies of commercial diesel can only be carried out by considering surrogate mixtures. N-heptane has been widely used as diesel fuel surrogate and its oxidation chemistry is extensively studied by plenty of groups[56,57,58] because it has a cetane number of approximately 56 (CN = 56), which is quite close to commercial diesel fuel. However, because of the complexity of diesel composition and reaction kinetics, the development of multi-component diesel surrogates, such as primary reference fuel (PRF)[59,60] and toluene reference fuel (TRF)[61,62] has received much attention.

The review highlights that the reaction mechanisms to describe the combustion chemistry of individual component in ABE-diesel blends are accessible. Some of them are well studied and widely validated if not all of them are. Table2 overviews all the base mechanisms adopted herein, including Pichon's mechanism[39] referred as NUI acetone mechanism, Black's mechanism[46] referred as NUI butanol mechanism and Marinov's mechanism[55] referred as LLNL ethanol mechanism, along with the proposed semi-detailed ABE-diesel mechanism. A reduced n-heptane mechanism [62] is extracted from the previous work in our group to represent diesel fuel herein to keep the simplicity for computational purpose as well as maintain the predictivity of this semi-detailed mechanism at the same time. The overall semi-detailed kinetic mechanism composes 262 species and 1509 reactions.