THE USE OF BA MIXTURE IN DIESEL ENGINES: BLEND PREPARATION, SPRAY VISUALISATION AND ENGINE PERFORMANCE

A Thesis submitted by

Sattar Jabbar Murad Algayyim

B. Eng., M.Sc. (Mech. Eng.)

For the award of

Doctor of Philosophy

2019

Abstract

The increasing energy demand and more stringent legislation on engine pollutant emissions with the use of carbon-neutral fuels have motivated the use of bio-alcohols such as butanol (B). Because butanol-acetone (BA) and acetone-butanol-ethanol (ABE) are intermediate mixtures in bio-butanol production, they present cost benefits compared to butanol production as a consequence of reduced energy consumption and recovery processes.

This study investigated the effect of using bio-alcohol additives with neat diesel (D) or biodiesel (Bd) on macroscopic spray characteristics, engine performance and emission concentration. The spray tests were carried out in a constant volume vessel (CVV) under different injection conditions using a high-speed camera. Engine tests were conducted using a single-cylinder direct injection (DI) diesel engine at three engine speeds (1400, 2000 and 2600 rpm) and two compression ratios (18:1 and 19:1) at full load.

Spray characteristics were altered to provide for more favourable combustion using bio-alcohol as an additive to D or Bd due to the low viscosity of bio-alcohol which resulted in increasing both the spray penetration length and spray volume. Therefore, spray atomisation and evaporation rates could be improved. Thus, an efficient diesel engine performance can be achieved as a result of controlling injection characteristics, especially when using a promising additive like butanol or BA blended with D or Bd.

Moreover, the experimental results of testing bio-alcohol with diesel showed that 10% normal-butanol-acetone (n-BA)-90% D blend showed a slight improvement in brake power (BP). The highest peak in-cylinder pressure was measured for the iso-butanol-acetone (iso-BA)-D blends and lower carbon monoxide (CO) emissions than those of the equivalent n-BA-D blend while nitrogen oxides (NO_x) and unburned hydrocarbons (UHC) emission levels of n-BA-diesel blends were lower than those of the equivalent iso-BA-D blends. By investigating the effects of n-BA and iso-BA-D blends on engine performance, the BA fermentation industry could be informed about the type of butanol that should be produced.

Because the different isomers of butanol have different beneficial effects on engine operation, blending them together as an additive could yield all the individual benefits of each isomer. Testing a dual blend of iso-butanol-normal-butanol (iso-B-n-B) blended with D showed that the high dual blend ratios of 10% and 13% iso-B produced higher peak in-cylinder pressures and heat release rates (HRR) as well as a substantial reduction in CO emissions. The higher blend ratios of 10% and 13% n-B produced much lower UHC emissions. A slight reduction was found in NO_x emissions when increasing either n-B or iso-B, with n-butanol slightly more effective. Therefore, a blend of n- and iso-butanol could be a promising alternative to a single isomer additive (iso/n-butanol) to optimise engine performance.

Finally, BA as an additive to neat cottonseed biodiesel has been investigated in relation to spray characteristics and engine performance. The experimental results of the BA-biodiesel blend revealed that the peak in-cylinder pressure for 30% BA was comparable to D and higher than that of neat Bd. BP was slightly improved for 10% BA at an engine speed of 2000 rpm while specific fuel consumption (SFC) was not significantly higher for any of the BA-Bd blends because of the smaller heating value of BA. Comparing the effect on emissions of adding BA to Bd, increasing the amount of BA reduced NO_x and CO compared to neat Bd, but increased UHC.

The BA blend was found to be the best additive for D or Bd fuel compared to ABE or B in related to production cost, blend properties, engine performance and emissions. Thus, the BA blend is promising as an alternative renewable environmentally friendly additive, blended with neat D or Bd without diesel engine modification that could enhance spray characteristics, improve engine performance and reduce diesel engine emissions.

Certification of Thesis

This Thesis is the work of ***Sattar Jabbar Murad Algayyim*** except where otherwise acknowledged, with the majority of the authorship of the papers presented as a thesis by publication undertaken by Student. The work is original and has not previously been submitted for any other award, except where acknowledged.

Student and supervisors' signature endorsement are held at USQ.

Sattar Jabbar Murad Algayyim

PhD Candidate Date

Associate Professor Andrew P. Wandel

Principal Supervisor Date

Professor Talal Yusaf

Associate Supervisor Date

Dr Ihsan Hamawand

Associate Supervisor Date

Statements of Contributions

The articles produced from this study were a joint contribution of the authors. The details of the scientific contribution of each author are provided below:

- **Article I: Algayyim, S. J. M**., Wandel, A. P., Yusaf, T., and Hamawand, I., *Production and application of ABE as a biofuel. Renewable and Sustainable Energy Reviews*, 2018. 82, Part 1: p. 1195-1214. :

  DoI: https://www.sciencedirect.com/science/article/pii/S1364032117313333

  The overall contribution of **Sattar Algayyim** was 60% to the concept development, analysis, drafting and revising the final submission; **Andrew Wandel, Talal Yusuf** and **Ihsan Hamawand** contributed to the remaining concept development, analysis, editing and providing important technical inputs by 25%, 5% and 10% respectively.

- **Article II**: **Algayyim, S. J. M**, Wandel, A. P., and Yusaf, T., The Impact of Injector Hole Diameter on Spray Behaviour for Butanol-Diesel Blends. *Energies*, 2018. 11(5): p.

  DoI: https://www.mdpi.com/1996-1073/11/5/1298

  The overall contribution of **Sattar Algayyim** was 65% to the concept development, analysis, drafting and revising the final submission; **Andrew Wandel** and **Talal Yusaf** contributed to the remaining concept development, analysis, editing and providing important technical inputs by 25% and 10% respectively.

- **Article III**: **Algayyim, S. J. M**., Wandel, A. P., Yusaf, T., Al-Lwayzy, S., and Hamawand, I., Impact of butanol-acetone mixture as a fuel additive on diesel engine performance and emissions. *Fuel*, 2018. 227: p. 118-126.

  DoI: https://www.sciencedirect.com/science/article/pii/S0016236118307245

The overall contribution of **Sattar Algayyim** was 60% to the concept development, analysis, drafting and revising the final submission; **Andrew Wandel, Talal Yusaf, Ihsan Hamawand** and **Saddam Al-Lwayzy** contributed to the remaining concept development, analysis, editing and providing important technical inputs by 20%, 10%, 5% and 5% respectively.

- **Article IV**: **Algayyim, S. J. M**., Wandel, A. P., Yusaf, T., and Hamawand, I., The impact of n-butanol and iso-butanol as components of butanol-acetone (BA) mixture-diesel blend on spray, combustion characteristics, engine performance and emission in direct injection diesel engine. *Energy*, 2017. 140(Part 1): p. 1074-10.

DoI: https://www.sciencedirect.com/science/article/pii/S0360544217315669

The overall contribution of **Sattar Algayyim** was 60% to the concept development, analysis, drafting and revising the final submission; **Andrew Wandel, Talal Yusaf** and **Ihsan Hamawand** contributed to the remaining concept development, analysis, editing and providing important technical inputs by 25%, 10% and 5% respectively.

- **Article V: Algayyim, S. J. M**., Wandel, A. P., Yusaf, T., Mixtures of n-butanol and iso-butanol blended with diesel: Experimental investigation of combustion characteristics, engine performance and emission levels in CI engine. *Biofuel*, 2018. pp. 1-10.

DoI: https://www.tandfonline.com/doi/abs/10.1080/17597269.2018.1493565

The overall contribution of **Sattar Algayyim** was 70% to the concept development, analysis, drafting and revising the final submission; **Andrew Wandel** and **Talal Yusaf** contributed to the remaining concept development, analysis, editing and providing important technical inputs by 25% and 5% respectively.

- **Article VI: Algayyim, S. J. M**., Wandel, A. P., Yusaf, T., and Al-Lwayzy, S., Butanol-Acetone Mixture Blended with Cottonseed Biodiesel: Spray Characteristics Evolution, Combustion Characteristics, Engine Performance and Emission. *Proceedings of the Combustion Institute*, 2018. 37: p. 1-11.

  DoI: https://www.sciencedirect.com/science/article/pii/S1540748918305777

  The overall contribution of **Sattar Algayyim** was 65% to the concept development, analysis, drafting and revising the final submission; **Andrew Wandel, Talal Yusaf** and **Saddam Al-Lwayzy** contributed to the remaining concept development, analysis, editing and providing important technical inputs by 25%, 5 % and 5% respectively.

Acknowledgements

My sincere gratitude and warm appreciation goes to:

Associate Professor **Andrew Wandel**, my principal supervisor: short sentences are not enough to acknowledge his contribution. The experience and expertise I have gained would not have been possible without his sound knowledge, positive attitude, technical support and valuable suggestions. His prompt response, easy access and open-door policy helped me to carry out my research within the required timeframe.

Professor **Talal Yusaf**, my associate supervisor: I am grateful for his sharing his long experience and his thoughtful guidance of and valuable suggestions about my research.

Dr **Ihsan Hamawand**, my associate supervisor: I am grateful for his guidance of and valuable suggestions about my research.

Dr **Saddam Al-Lwayzy**, Dr **Rishabh Choudhury**, Dr **Paul Baker**, Mr **Robert Kimber** and Mr **Brian Lenske** (USQ staff) for assisting with experiments and helpful discussions.

Dr **Rachel King** for her assistance with the statistical analysis, Dr **Barbara Harmes** for English support and Mrs **Weide Wandel** for proofreading this thesis.

I would like to express my greatest appreciation to the **Ministry of Higher Education Iraq** which sponsored my studies. Without them, I would not have been able to achieve my goal.

I acknowledge my sincere indebtedness and gratitude to my parents, wife, brothers, sisters and daughters, son and friends for their prayers, sacrifices and moral support given to me.

Table of Contents

Nomenclature

ABE	acetone-butanol-ethanol mixture
AFEX	ammonia fibre/freeze explosion
ASOI	after start of injection
B	100% butanol
BA	butanol-acetone mixture
Bd	biodiesel
10BA90Bd	10% normal-butanol-acetone 90% biodiesel
20BA80Bd	20% normal-butanol-acetone 80% biodiesel
30BA70Bd	30% normal-butanol-acetone 70% biodiesel
B20D80	20% butanol 80% diesel
10n-BA90D	10% normal-butanol-acetone 90% diesel
20n-BA80D	20% normal-butanol-acetone 80% diesel
10iso-BA90D	10% iso-butanol-acetone 90% diesel
20iso-BA80D	20% iso-butanol-acetone 80% diesel
5iso-B-5n-B-90D	5% iso-butanol-5% normal-butanol 90% diesel
7iso-B-13n-B-80D	7% iso-butanol-13% normal-butanol 80% diesel
10iso-B-10n-B-80D	10% iso-butanol-10% normal-butanol 80% diesel
13iso-B-7n-B-80D	13% iso-butanol-7% normal-butanol 80% diesel
B40D60	40% butanol 60% diesel
BMEP	brake mean effective pressure
BP	brake power
BSFC	brake-specific fuel consumption
BSH	barley straw hydrolysate
BTE	brake thermal efficiency
C_p	specific heat at constant pressure
C_v	specific heat at constant volume

CAD	crank angle degree
CCD	charge-coupled device
CFD	computational fluid dynamics
CI	compression ignition
CN	cetane number
CO	carbon monoxide
CO_2	carbon dioxide
CVV	constant-volume vessel
D100	100% diesel
DI	direct injection
DOC	diesel oxidation catalyst
EGR	exhaust gas recirculation
EGT	exhaust gas temperature
HRR	heat release rate
HVO	hydrotreated vegetable oil
IBE	isopropanol-butanol-ethanol
ICE	internal combustion engine
IP	injection pressure
isoB	iso-butanol
MFB	mass fraction burnt
nB	normal butanol (n-butanol)
NO_x	nitrogen oxides
PM	particulate matter
rpm	revolutions per minute
S	spray tip penetration
secB	secondary butanol
SI	spark ignition

SOI	start of injection time
T	torque
tertB	tertiary butanol
TDC	top dead centre
THC	total hydrocarbon
UHC	unburned hydrocarbons
V	spray volume
γ	ratio of specific heats
ϕ	equivalence ratio
θ	spray cone angle

Chapter 1 - Introduction

1.1 Background

Significant energy demands from population growth (Figure 1) together with environmental concerns have led many countries to look for renewable, sustainable, economically feasible and environmentally friendly energy resources. For these reasons, there is high motivation to use biofuels. Figure 2 presents and predicts the increase in biofuel production in the world. There are several kinds of biofuel that have been used, but the main biofuels being investigated by researchers are biodiesel and bio alcohol (Savaliya et al. 2013; Algayyim et al. 2017; Algayyim, S. et al. 2018; Algayyim, S. J. M., Wandel, A. P., Yusaf, T., Al-Lwayzy, S. 2018; Algayyim, S. J. M., Wandel, A. P., Yusaf, T., Al-Lwayzy, S., et al. 2018; Algayyim, S. J. M., Wandel, A. P., Yusaf, T., Hamawand, I. 2018; Emiroğlu & Şen 2018; Joy et al. 2018). Depending on climate, soil condition and available manufacturing, each country is capable of producing biodiesel and bio alcohol from agricultural residues from its available land mass (No 2011). As a result of the large amount of biomass produced annually, alternative fuels such as biodiesel and bio-alcohol can be produced easily and cheaply. Australia has a large agricultural sector and there are plentiful supplies of various kinds of biomass residues from agriculture such as cottonseed, wheat straw, barley straw, sugar cane and corn stover (Koçak et al. 2007). This abundance of raw materials and biomass encourage researchers to investigate their biofuel potential. This could make the national economy less dependent on imported fossil oils.

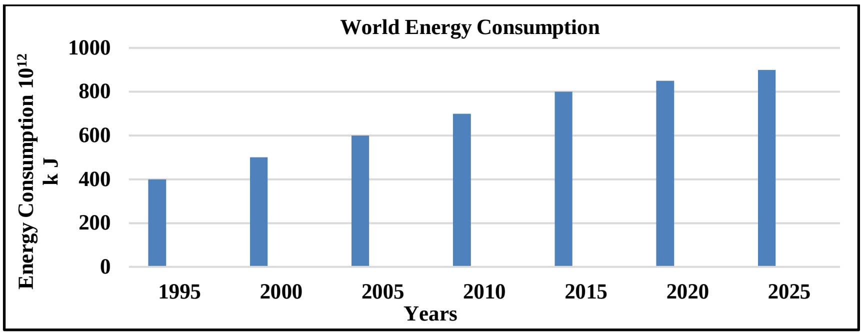


Figure 1. World energy consumption. Adapted from Erski (2014).

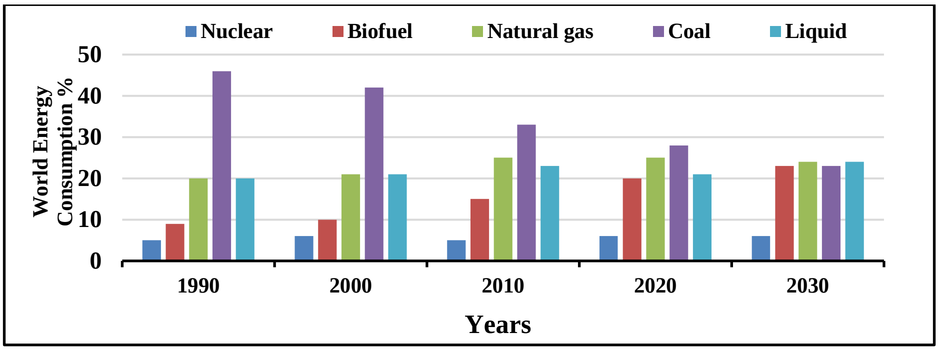


Figure 2. World energy consumption and how biofuel dramatically increases in coming years. Adapted from Erski (2014).

The current issue with using biodiesel as an alternative fuel for Compression Ignition (CI) engines is unfavourable fuel properties such as high density and viscosity, which cause obstacles in completing fuel atomization and combustion (Koçak et al. 2007). Another problem caused by using biodiesel is higher NO_x emissions, which increase health problems (Xue et al. 2011; Wu & Wu 2013).

Bio-alcohols derived through biochemical processes from different biomass resources have a high oxygen content, which helps to complete the combustion of conventional fuel (Campos-Fernández et al. 2012). Particularly, ethanol and methanol with diesel or biodiesel have been extensively investigated. Experimental studies on ethanol use in diesel engines have been carried out by a number of researchers (Satgé de Caro et al. 2001; Hansen et al. 2005; Hansen et al. 2006; Zannis et al. 2007; Kumar et al. 2013; Shahir et al. 2015; Tse et al. 2015). However, some studies revealed some disadvantages of using ethanol and methanol as a blend for diesel engines due to:

1. Poor blending solubility and limited miscibility in diesel fuel and phase separation, especially at low temperatures (Sayin 2010).

2. Unsuitable fuel properties for diesel engine design such as the lower cetane number, lubricity, and heating value of ethanol (Jin, Yao, Liu, Lee et al. 2011).

3. Production methods for first-generation biofuel (edible crops used to produce bioethanol may lead to shortages of food and result in increased food prices) (Juan et al. 2011).

Therefore, researchers have started focussing on the use of butanol as a suitable blend for diesel engines (Laza & Bereczky 2011). Butanol presents a number of advantages compared with ethanol: it has a higher cetane number (CN) (25), lower kinematic viscosity (2.63 mm^2/s) and higher heating value (33,100 kJ/kg). These benefits can be utilised to improve the properties of fuel blends, so butanol as a potential second-generation biofuel is a popular and competitive alcohol blend for diesel. These benefits can contribute to providing power similar to regular diesel fuel while producing less emissions (Weerachanchai et al. 2009; Lujaji et al. 2010; Doğan 2011; Yilmaz et al. 2014). However, the cost of butanol production (Figure 3) is the main issue of using it as fuel in internal combustion (IC) engines. Because of the high recovery and purification costs, other fermentation products such as acetone, butanol and ethanol (ABE) (the intermediate outcome during the production of butanol) have been proposed to be used as an alternative alcohol blend. ABE is typically produced in the ratio of 3:6:1 with varying concentrations when using traditional batch fermentation (Qureshi et al. 2010). Li et al. (2014) found that a mixture of butanol and acetone with no ethanol can be produced from the fermentation process. A butanol-acetone ratio of 2.9:1 can be produced when cassava is used as substrate in the fermentation (Li et al. 2014).

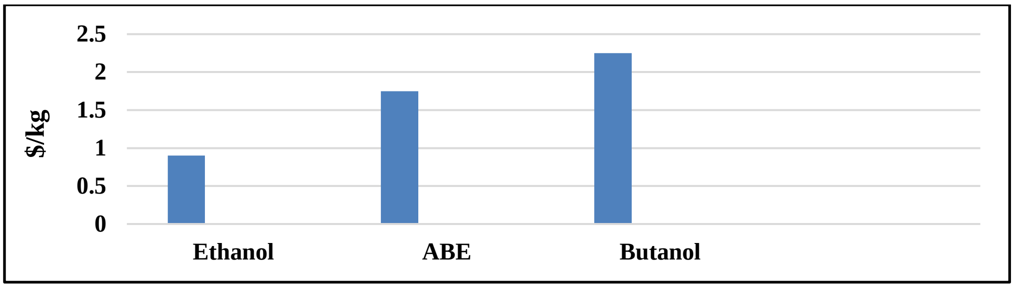


Figure 3. The production cost compared between ethanol, butanol and ABE. Adapted from Jin, Yao, Liu, Lee et al. (2011).

1.2 Research Questions

This thesis addresses the following questions:

1. What is the challenge of ABE production and its application as a fuel for internal combustion engines (ICE)?
2. What are the effects of varying concentrations of bio-alcohol additives on spray characteristics when:
    a) using butanol (B) blended with diesel?
    b) using butanol-acetone (BA) blended with diesel?
    c) using a specific isomer of butanol mixed with acetone [iso-butanol-acetone (iso-BA) or n-butanol-acetone (n-BA)] blended with diesel?
    d) using butanol-acetone (BA) blended with cottonseed biodiesel?
3. What are the effects of varying concentrations of bio-alcohol additives on engine performance and emissions when:
    a) using BA blended with diesel?
    b) using iso-BA or n-BA with diesel?
    c) using blends of isomers of butanol (iso- B and n-B) with diesel?
    d) using BA blended with cottonseed biodiesel?

1.3 Overall Research Aim

The research aim is to develop an understanding of the behaviour of a renewable, sustainable and commercially-feasible alternative fuel – with similarities to conventional fuel properties – in order to determine how its spray should be injected into an engine and evaluate the performance and emissions when the alternative fuel is used in a diesel engine.

1.4 Objectives

The objectives of this study are to:

1. Review and summarise the production and application of ABE as fuel for ICEs.
2. Investigate the impact of injector hole diameter and ambient conditions on spray penetration length, spreading angle and spray volume when using bio-alcohol blended with diesel under different injection conditions at atmospheric pressure and temperature.
3. Evaluate diesel engine performance and emissions when using BA blended with diesel.
4. Investigate and compare the spray penetration length, spreading angle and spray volume, engine performance and emissions when using n-BA or iso-BA blended with diesel.
5. Evaluate the diesel engine performance and emissions when using a mixture of n-butanol-iso-butanol blended with diesel.
6. Examine the spray behaviour, engine performance and emissions when using butanol-acetone (BA) blended with biodiesel.

1.5 Thesis Structure

This thesis is comprised of an introduction that highlights the background and research theme, an extensive review of literature that addresses the novelty of the study (**Article I**), five major studies that cover the other five objectives (**Articles II–VI**), supported by additional studies (**Appendices A.1-2**) and a conclusion that summarises the findings and contributions of this study with future recommendations. A total of six journal articles produced from this research are presented below:

Article from study 1:

Article I: Algayyim, S. J. M., Wandel, A. P., Yusaf, T., and Hamawand, I., Production and application of ABE as a biofuel. *Renewable and Sustainable Energy Reviews*, 2018. 82, Part 1: p. 1195-1214.

Article from study 2:

Article II: Algayyim, S. J. M, Wandel, A. P. and Yusaf, T., The Impact of Injector Hole Diameter on Spray Behaviour for Butanol-Diesel Blends. *Energies*, 2018. 11(5): p. 1298.

Article from study 3:

Article III: Algayyim, S. J. M., Wandel, A. P., Yusaf, T., Al-Lwayzy, S., and Hamawand, I., Impact of butanol-acetone mixture as a fuel additive on diesel engine performance and emissions. *Fuel*, 2018. 227: p. 118-126.

Article from study 4:

Article IV: Algayyim, S. J. M., Wandel, A. P., Yusaf, T., and Hamawand, I., The impact of n-butanol and iso-butanol as components of butanol-acetone (BA) mixture-diesel blend on spray, combustion characteristics, engine performance and emission in direct injection diesel engine. *Energy*, 2017. 140 (Part 1): p. 1074-10.

Article from study 5:

Article V: Algayyim, S. J. M., Wandel, A. P. and Yusaf, T., Mixtures of n-butanol and iso-butanol blended with diesel: Experimental investigation of combustion characteristics engine performance and emission levels in CI engines. *Biofuel*, 2018, pp. 1-10.

Article from study 6:

Article VI: Algayyim, S. J. M., Wandel, A. P., Yusaf, T. Al-Lwayzy, S., Butanol-Acetone Mixture Blended with Cottonseed Biodiesel: Spray Characteristics Evolution, Combustion Characteristics, Engine Performance and Emission. *Proceedings of the Combustion Institute* (2018), https://doi.org/10.1016/j.proci.2018.08.035

In addition to these journal articles which comprise the main body of the thesis, conference paper and abstract are included in Appendix A to provide a comprehensive coverage of the research aim and objectives of this thesis.

The engine performance of hydrated butanol-acetone (BA) and diesel blend are provided in **Appendix A.1.** The spray characteristics and engine performance of ABE blended with diesel is provided in **Appendix A.2.** Fundamental equations related to engine volume calculation are provided in **Appendix B**.

The first study **(Article I) (Chapter 2)** reviews the recent developments, challenges and future prospects of butanol and ABE production and consequential application as fuel.

The **second objective (Chapter 3)** of this study, to evaluate and investigate the impact of injector hole diameter and injection conditions on spray characteristics of butanol-diesel blend under different injection conditions, is principally met by **Article II.**

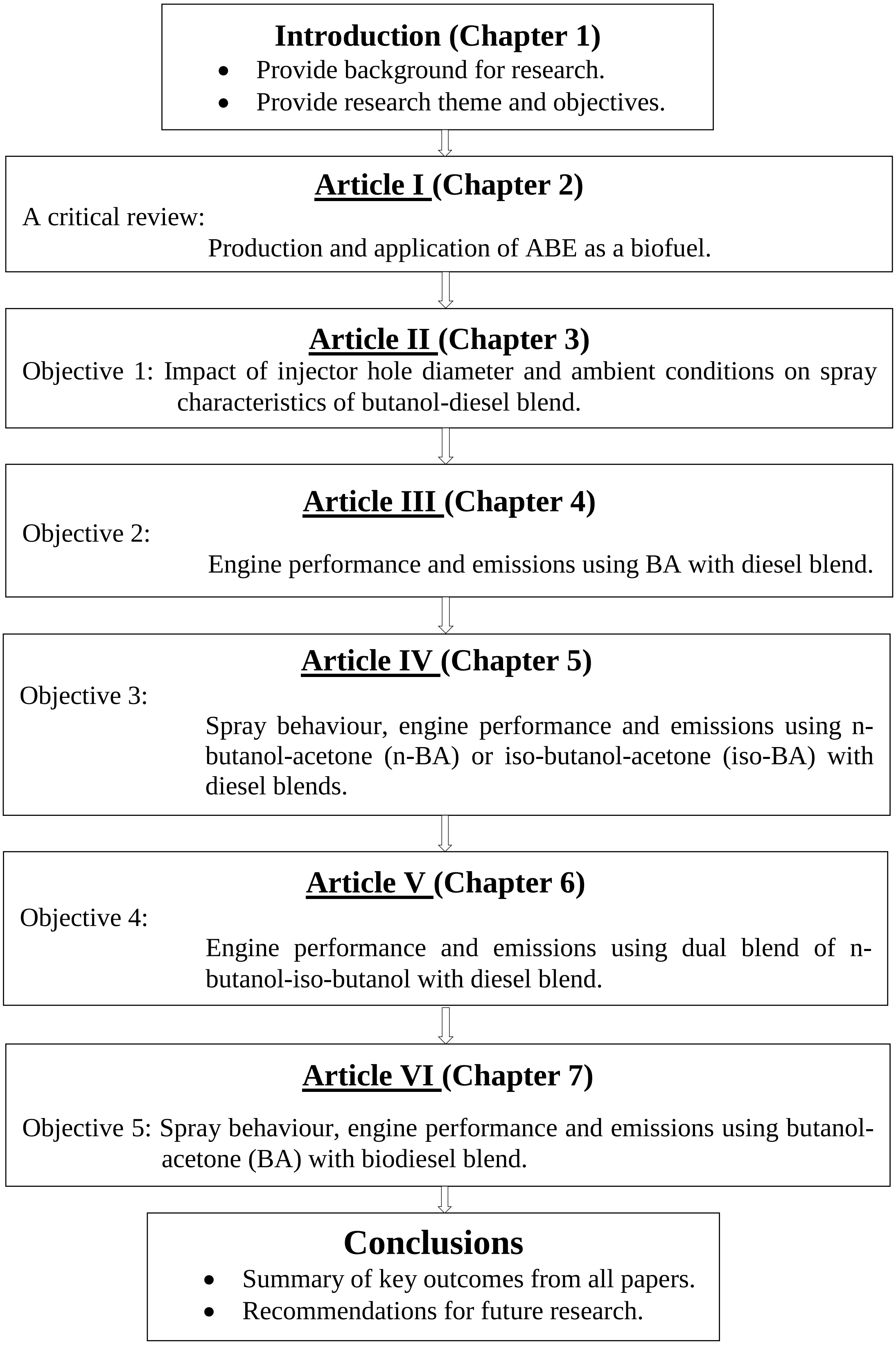
The **third objective (Chapter 4)** (performance and emissions of an engine using BA as an additive to diesel fuel), to our knowledge, has not yet been investigated, and is met by **Article III.**

The **fourth objective (Chapter 5)** of this study, to investigate and compare the usage of either iso-butanol or n-butanol in a BA mixture blended with neat diesel, is met by **Article IV**.

The **fifth objective (Chapter 6)** of this study ,to evaluate and analyse the effect of using a dual blend of iso-butanol and n-butanol with neat diesel in a CI engine by studying the performance of the diesel engine, is presented in **Article V.**

The **sixth objective (Chapter 7),** using a BA blend as an additive to biodiesel fuel is addressed in **Article VI.**

The structure of the thesis is represented in Figure 4.



Introduction (Chapter 1)

- Provide background for research.
- Provide research theme and objectives.

Article I (Chapter 2)

A critical review:
Production and application of ABE as a biofuel.

Article II (Chapter 3)

Objective 1: Impact of injector hole diameter and ambient conditions on spray characteristics of butanol-diesel blend.

Article III (Chapter 4)

Objective 2:
Engine performance and emissions using BA with diesel blend.

Article IV (Chapter 5)

Objective 3:
Spray behaviour, engine performance and emissions using n-butanol-acetone (n-BA) or iso-butanol-acetone (iso-BA) with diesel blends.

Article V (Chapter 6)

Objective 4:
Engine performance and emissions using dual blend of n-butanol-iso-butanol with diesel blend.

Article VI (Chapter 7)

Objective 5: Spray behaviour, engine performance and emissions using butanol-acetone (BA) with biodiesel blend.

Conclusions

- Summary of key outcomes from all papers.
- Recommendations for future research.

Figure 4. Flow diagram of this thesis.

Chapter 2 - Production and Application of ABE as a Biofuel

2.1 Article I

Algayyim, S. J. M., Wandel, A. P., Yusaf, T., and Hamawand, I., *Production and application of ABE as a biofuel. Renewable and Sustainable Energy Reviews,* 2018. 82, Part 1: pp. 1195-1214.

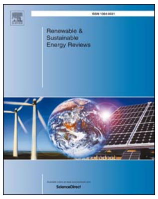
Article I (Chapter 1) extensively reviews the production and application of ABE as a biofuel. Firstly, the study summarises the production history of ABE and its associated processes. Secondly, current substrate types used as raw material to produce ABE have been detailed and the quantity of yield produced from these biomasses have also been reviewed and compared. Using lignocellulosic biomass as a source of fermentation is complex because it is difficult to ferment. Pre-treatments have to be used to increase the yield amount of butanol. Different pre-treatment methods have been summarised and addressed. Furthermore, applications of three kinds of biofuel (ethanol, butanol and ABE) have been extensively reviewed and summarised relating to properties, combustion behaviour, engine performance and emissions levels as a sole fuel or as an additive in CI and SI engines.

Renewable and Sustainable Energy Reviews 82 (2018) 1195–1214

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



Production and application of ABE as a biofuel

Sattar Jabbar Murad Algayyim[a,d,*], Andrew P. Wandel[b], Talal Yusaf[a], Ihsan Hamawand[c]

[a] School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, QLD 4350, Australia
[b] Computational Engineering and Science Research Centre, School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, QLD 4350, Australia
[c] National Centre for Engineering in Agriculture, University of Southern Queensland, Toowoomba, QLD 4350, Australia
[d] Department of Mechanical, College of Engineering, University of Al-Qadisiyah, Al-Diwaniyah, Iraq

ARTICLE INFO

Keywords:
Biofuel
Acetone-butanol-ethanol
ABE fermentation
Lignocellulosic
clostridium
Substrate
Diesel and gasoline fuel

ABSTRACT

The increasing energy demand and more stringent legislation for engine pollutant emissions with the use of carbon-neutral fuels have forced to use alcohol. ABE, a combination of acetone, butanol, and ethanol, is a potentially fuel that can be produced from waste biomass via fermentation. Recently, this fuel has attracted researchers' attention due to its better performance and less emission as a diesel blend when compared to ethanol. First, this article addresses past and recent research conducted in the field of biofuel (ABE) production from lignocellulosic materials. Second, the development in ABE production efficiency is reviewed and various methods of improving ABE production are presented. ABE from lignocellulosic materials (a green energy resource) can be improved through metabolic engineering of the fermenting yeast (*Clostridia)* and/or pre-treatment techniques. Furthermore, the application of ethanol, butanol and ABE as biofuel blends is compared and summarised considering three aspects (1) combustion characteristics; (2) as an additive blend of diesel fuel in compression engines; and (3) as an additive blend of gasoline in spark ignition engines related to engine performance and emission levels.

This study shows that ABE has the potential to become an important second-generation biofuel that can be blended with diesel and gasoline for the following reasons: it is cheaper to produce compared to butanol, it is possible to improve engine performance and it reduces exhaust gas emissions. Moreover, engine power is comparable to diesel, and at the same time ABE releases fewer emissions such as CO and NO_x than other fuel blends.

1. Introduction

Due to population growth along with environmental concerns there is significant demand for carbon-neutral fuels in addition to more stringent legislation governing engine pollutant emissions. This has been attracting new interest in renewable, sustainable and environmentally friendly energy resources. Biomass resources such as biomass waste from agricultural industry are available widely and can be converted to different biofuel type [1,2]. Because of the large amount of biomass produced annually, biofuel has a potential to be produced easily and cheaply. There are plentiful supplies of various kinds of biomass (residues from agriculture) such as wheat straw, barley straw, corn fibre, bagasse and corn Stover [3–6]. The potential conflict between food and fuel will be reduced by using agricultural waste and residues as raw material substrate for alcohol fermentation. This abundance of waste biomass has encouraged researchers and investors to convert it to biofuel, which contributes considerably to make economies less dependent on imported fossil fuels. Depending on climate, soil condition, and available manufacturing, each country is capable of producing biofuel from agricultural residues with respect to its available landscape [7]. Moreover, stricter environmental legislation because of using fossil fuels also plays a crucial role in reinforcing the production and utilisation of biofuels. As reported, there is noticeable motivation for the use of alcohol [8].

Biofuels are classified into two types, primary and secondary. The first type of biofuel is used directly without modification for heating or cooking such as grass, wood chips, and wood. By treating biomass, the secondary type of biofuel is made such as ethanol, butanol, and mixtures such as acetone-butanol-ethanol (ABE). The secondary type of biofuel is also divided into first, second, and third generation biofuel depending on the biomass and technological process utilisation for their production. First-generation biofuels are the type of liquid fuels (predominantly ethanol) that are normally produced from sugars [9,10], grains or seeds [11,12] and require simple technique to produce the

---

[*] Corresponding author at: School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, QLD 4350, Australia.
E-mail address: Sattarjabbarmurad.algayyim@usq.edu.au (S.J.M. Algayyim).

http://dx.doi.org/10.1016/j.rser.2017.09.082
Received 14 September 2016; Received in revised form 12 July 2017; Accepted 24 September 2017

Nomenclature

ABE	Acetone-butanol-ethanol
AFEX	ammonia fibre/freeze explosion
BA	Butanol-acetone
BMEP	brake mean effective pressure
BSFC	brake specific fuel consumption
BP	brake power
BaPeq	toxicity equivalent of phase
BSH	barley straw hydrolysate
BTE	brake thermal efficiency
CAD	crank angle degree
CFD	computational fluid dynamic
CI	compression ignition
CO	carbon monoxide
CO_2	carbon dioxides
CN	cetane number
CFR	cooperative fuels research engine
CFPP	cold filter plugging point
Cn	crude canola
Cr	corn
DI	Direct injection
DOC	diesel oxidation catalyst
EGR	exhaust gas recirculation
ϕ	equivalence ratio
FAME	fatty acid methyl esters
FILE	forward illumination light extinction
HMF	hydroxyethyl furfural
Hn	hazelnut oil
MFB	mass fraction burnt
NO_x	nitrogen oxides
nB	normal butanol
Ol	olive
OSU	Ohio state university
PAHs	polycyclic aromatic hydrocarbons
PM	particulate matter
RPM	revolution per minute
RSO	rapeseed oil
S	spray tip penetration
S_u	laminar burning velocity
SI	spark ignition
Sb	soybean
SF	sun- flower
Sf	flame speed
T_b	flame temperature
THC	total hydrocarbon
WS	wheat straw

final biofuel product. Six-carbon sugars (mainly glucose) in starch can easily be converted to ethanol by the use of *Clostridiums* (yeast) because starch is much easier to ferment than cellulose. For second–generation liquid biofuels, there are two different methodologies that can be used to produce them (thermal processing and biochemical). Waste biomass is either non-edible residues of crop production or non-edible residues of industrial plant. Lignocelluloses biomass can be converted to glucose in different processes. A great deal of research addresses the production of ethanol from biomass waste [13–16] because food crops such as corn and sugarcane are insufficient to meet the world demand for ethanol. Lignocellulosic biomass are proposed to be alternative source for commercially ethanol production. The complex carbohydrate molecules containing cellulose and hemicellulose can be broken down by enzyme-catalysed hydrolysis into simple sugar resulting from pre-treatment. Pre-treatment is a method designed to facilitate the separation of cellulose, hemicellulose and lignin to simple sugars (Fig. 4). Moreover, the development of genetic engineering can also enhance the biofuel yield amount via fermentation. These processes use different types of anaerobic bacteria such as the solvent organic *Clostridia;* and are capable of converting a wide range of carbon sources (e.g. glucose, galactose, cellobiose, mannose, xylose and arabinose) to fuels such as ABE [17]. Hence, the use of lignocellulosic biomass via fermentation to produce ABE or BA is a good way to meet butanol or ABE world needs in the world. Butanol is produced after separating it from the fermentation product, which can be either ABE or butanol-acetone (BA) mixture depending on the fermentation process conditions. It is produced by the anaerobic conversion of carbohydrates by strains of *Clostridium acetobutylicum* into ABE as *clostridia* secrete accommodates the breakdown of polymeric carbohydrates into monomers [18–20]. Because of the high cost of separating butanol from these mixtures, using ABE or BA as biofuel is an alternative way to reduce the overall cost. Furthermore, third-generation biofuels, specifically derived from microbes and microalgae, are considered to be a possible alternative energy resource to back up the first and second-generation biofuels [1]. However, these techniques are still in the early stages and more investigations are needed. The main goal of this paper is to present the latest development in research related to ABE production and to address the feasibility of the production process. In addition, this article addresses the potential application of the alcohols such as ethanol, butanol, and ABE as a fuel and/or an additive for internal combustion engines (Figs. 1–3).

2. ABE production

2.1. ABE production history

In 1911, Strange Company & Graham Ltd, together with Professor William Perkin from Manchester University and his assistant Chaim Weizmann attempted to solve the issue of increasing alcohol production by isolating a bacterium strain that produced 3-methylbutanlol (isoamyl alcohol). This strain was later named *Clostridium acetobutylicum.* The first production plant which produced acetone from starch came from this development [26,27].

In 1916 and 1917, alcohol production technology had also been transferred to Canada and the United States, respectively, due to the lack of the substrate maize in England [27]. During World War I, the high needs of cordite (smokeless gun powder), which requires acetone for its production made acetone the desired product of the fermentation process [28]. In 1945, biotechnological processes supplied 66% of the total butanol production and 10% of the total acetone production. In the 1920s, the growing vehicle industry required a high amount of

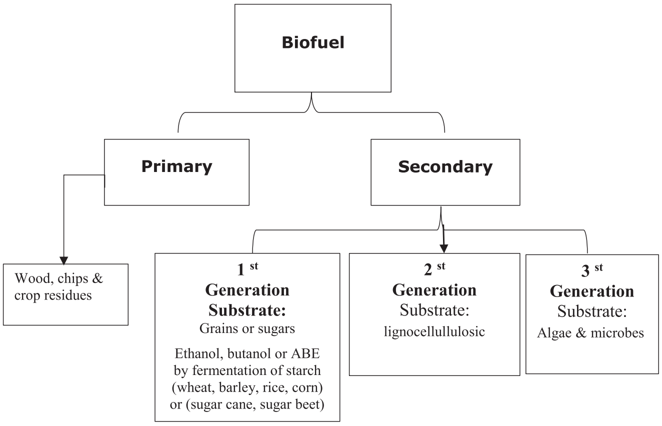


Fig. 1. Classification of biofuel adapted from [21].

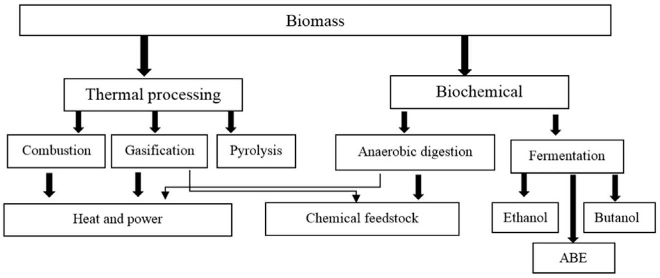


Fig. 2. Thermal processing and biochemical methodologies used to produce biofuel from biomass adapted from [22].

butanol production, and butanol and butyl acetate were found to have good properties as solvents for the quick-drying polishes for the finishing of cars. Because more cars were produced, there was an increased demand for butanol production within the fermentation industry [29].

During World War II, the increased energy demands were linked with the fermentation industry [30]. However, soon after 1945 and due to the economic competitiveness butanol produced from the petrochemical industry resulted in a drop in the fermentation industry. In the 1950s and 1960s, in Europe and North America the fermentation industry completely stopped due to economic competition from the petrochemical industry; increased substrate prices; and low productivity yields. In the 1950s, in China, an ABE fermentation process started and it peaked in the 1980s. However, the ABE fermentation was ended at the end of the last century when all ABE plants were closed because of competitive influence of the increased petrochemical industry [31]. China also developed its ABE process industry from C. *Acetobutylicum* strains using generally starch-based biomass [32]. Recently, China has been re-established ABE production with approximately eleven production plants currently in operation and another number of plants are under construction [32].

In the 1980s and 1990s, research into the progress of the ABE process has markedly increased and feasibility studies have been carried out in France and Austria [32]. In France, production of additive alcohols for gasoline fuel from cereal straw, corn Stover, and sugar beet as substrate of fermentation is commercially evaluated. In addition, potatoes were also utilised as biomass sources (substrate) for fermentation in Austria. Recently, many companies such as DuPont, BP and GEVO have initiated projects to produce butanol from renewable biomass. In 2006, BP and DuPont announced their partnership to develop and commercialize butanol from biomass; and planned to produce 300,000 t per year [33]. In 2008, investigation results from BP and DuPont proposed that the use of butanol could increase the butanol blending in gasoline fuel [33]. In 2009, the partnership was cleared to take over the US company butanol LLC. On 25 September 2009, BP and Mazda announced an ethanol and butanol blend would be used in the Petit Le Mans Race, USA [1]. Currently, the ABE fermentation industrial has been re-established. However, these plants operate only in some plants in some place in the word such as China and Brazil. Table 1 presents a summary of ABE production industry in some place throughout the world during the period 1920–2014. The economic feasibility of ABE fermentation is governed by three important factors: cost of raw material; production yield and solvent recovery. Thus, it can be concluded that these studies showed fluctuations in the ABE industry in the past; however, recently, there has been a significant growth in

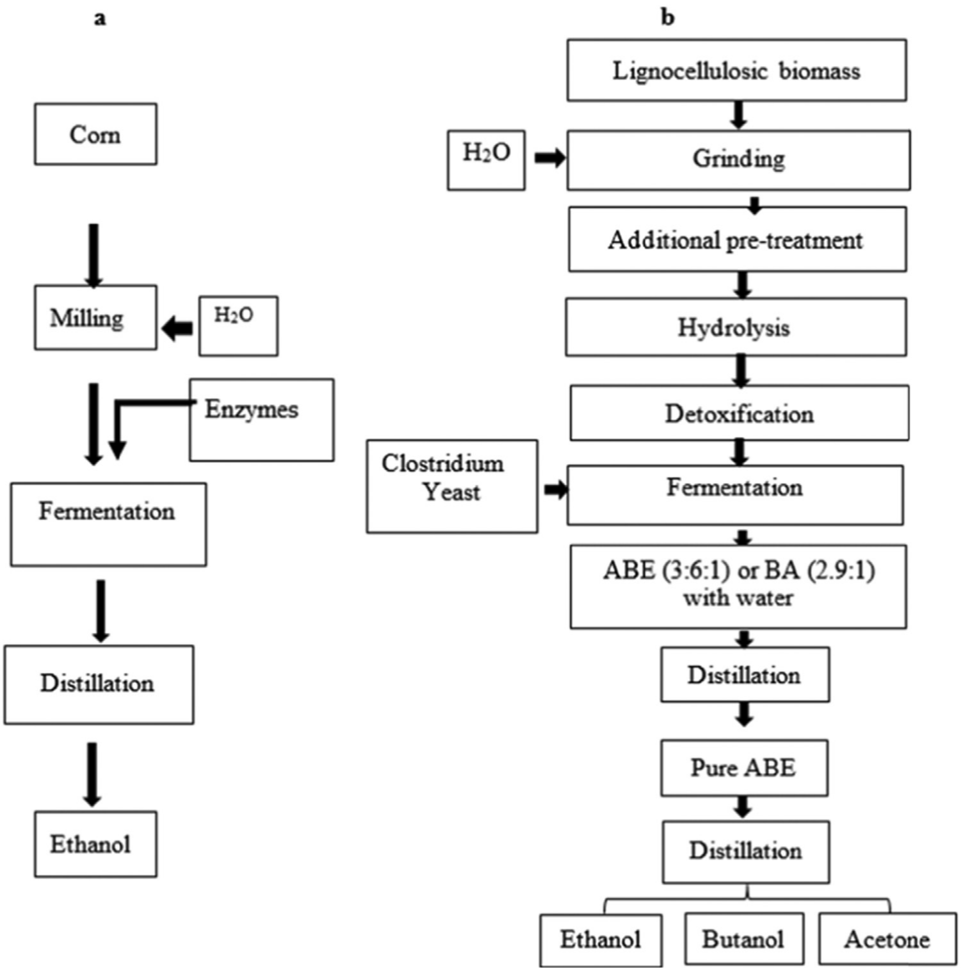


Fig. 3. Ethanol production way adapted from [23] butanol and ABE production process from lignocellulosic biomass with pretreatment adapted from [24,25].

Table 1
Production of ABE industry in some parts of the world during the period 1920–2014 adapted from [25].

Author	Year	Location	Substrate	Refs.
Crawford (1930)	1913–1914	Rainham & England	Potato starch	[29]
Jones et al. (2000)	1923–1935	Peoria & USA	Corn starch & molasses	[34]
Nimcevic & Gapes (2000)	1930	Philadelphia, Puerto Rico, USA, India & Australia	Corn starch & molasses	[35]
Zverlov et al. (2006)	1929–1935	Dokshukino, Grosnyi Talitsk & USSR	Starch, wheat flour & molasses	[30]
Chiao & Sun (2007)	1960	Shanghai, Beijing & Wuxi, China	Corn starch & cassava	[31]
Ni & Sun (2009)	1965–1970	Zhejiang, Tianjin & Yunnan, China	Corn, corn starch & cassava	[32]
Chiao & Sun (2007)	1980^{s}	Hebei & Shandong, China	Different lignocellulosic biomass	[31]
Joins Novozymes (2008)	2008	USA & Japan	Different lignocellulosic biomass	[33]
Savaliya et al. (2013)	2014	SaBuCo Jubail & Saudi Arabia	Different lignocellulosic biomass	[1]

the ABE industry in the world due to the genetic engineering enhancement.

2.2. Current ABE production related to substrate types

ABE can be produced from different types of substrate derived from both edible feedstock, and non-edible feedstock wastes of agricultural and industry residues such as corn, corn Stover, corn fibre, rice straw, sugar beet pulp, surplus dates, packing peanuts, orchard waste and marine macro algae. The high price of feedstocks and food scarcity are the main issues of the commercial ABE production from food crops such as corn [36–38]. Therefore, the utilisation of low price lignocellulosic biomass is one of the main ways considered to overcome the cost of the substrate [37,39,40]. As a result, researchers are focusing on using non-edible feedstock. Lignocellulosic biomass, has been utilised for bioenergy production because it is an abundant material; it is an inexpensive stored renewable energy form of carbon source; and does not compete with human food [38]. A variety of lignocellulosic materials have been employed for the production of ABE [4,39]. Using cheaper agricultural residues or waste can lead to significant reductions in production cost and may enable ABE to compete with ethanol in the biofuel market [30]. Sweet sorghum bagasse, a high biomass and sugar yield crop containing approximately equal quantities of soluble and insoluble compounds, i.e. glucose, sucrose, cellulose and hemicellulose is considered to be a promising an alternative substrate for alcohol [41]. This substance is useful for industrial processes because it converts the residues of biomass to liquid alcohol. Moreover, ABE fermentation from lignocellulosic residue is more economically friendly than sugar or starch based fermentation on the feedstock stage [42]. Another study using lignocellulosic feedstock of jatropha seed cake was undertaken by a researcher [43]. They used *Clostridium acetobutylicum* as a yeast strain for the fermented [43]. Fermentation was supported by acid pre-treated to optimise the yield of ABE production. Li et al. [44] studied the effect of the Clostridium acetobutylicum Mutant (ARTI8) at atmospheric and room temperature plasma in ABE yield. The result showed higher butanol production than that of wild-type strain. The butanol yield was 11.3 g L^{-1}, 31% higher than that of the wild-type strain when it used for ABE fermentation. The study also showed the effect of cassava starch flour concentration, pH regulator, and vitamins on ABE production. The highest butanol production achieved with 15.8 g L^{-1} and butanol yield 0.31 g/g as a result of optimizing the factors above. Furthermore, ABE fermentation using ART18 yeast strain was conducted. The butanol productivity was 16.3 g L^{-1} with 0.28 g L^{-1} h^{-1}, which means ART18, is a powerful strain in the ABE fermentation industry.

Zhange et al. [4] produced ABE from the corncob residue by using *Beijerinckii* NCIMB 8052. Detoxification using $Ca(OH)_2$ was utilised to remove inhibitors resulting in an ABE yield of 0.32 g/g and a productivity of 0.33 g L^{-1} h^{-1}. Qureshi et al. [38] reported that ABE yield ranging from 0.35 g/g to 0.39 g/g production by C. *beijerinckii* BA101 was obtained from fermentation of corn fiber hydrolysate treated with sulfuric acid. Furthermore, He and Chen [37] improved the fermentation production efficiency of lignocellulose by alkali-steam-exploded corn Stover (SECSAT) with *Clostridium acetobutylicum* ATCC 824 strain. The results showed that the production ratio of acetone was promoted; and the production ratio of ethanol was lower compared to without pre-treatment. By using pre-treatment alkali-steam-exploded (ASE) corn Stover, ABE concentration is increased is by 71%. It also obtained a significant increase in area proportion of fibre cells from 53% to 90%. The fermentation efficiency by ASE could not only increase the ABE yield, but could also change the solvent ratio, which means that the solvent ratio can easily be controlled by controlling the pre-treated step. Table 2 shows different biomass types utilised as a substrate for ABE fermentation. The current production of ABE presents a significant enhancement in yield compared to the traditional fermentation. The enhancement in yield increased as a result of developing fermentation techniques.

2.3. Improving substrate utilisation by pre-treatment technique

Wide research has been employed on enhancing the fermentation yield and product recovery techniques for ABE [57,58]. Agricultural

Table 2
The quantity of ABE produced from variety biomasses, organized by increasing ABE production.

Author	Type of biomass	Yield ABE (g/g)	Refs
Moradi et al. (2013)	Rice straw by acid and alkaline pre-treatments	0.064	[45]
Yang et al. (2015)	Dilute sulfuric acid-pre-treated barley straw which improves enzymatic sugar production	0.135	[46]
Huesemann et al. (2012)	Brown microalgae biomass	0.16	[47]
Qureshi & Blaschek (2001)	Corn	0.21	[48]
Kheyrandish et al. (2015)	Potato waste starch	0.26	[49]
Zhang et al. (2014)	Corn Stover by alkaline twin-screw extrusion pre-treatment	0.286	[6]
Ezeji & Blaschek (2008)	Fermentation of dried distiller's grains and soluble hydrolysates	0.31	[50]
Yang et al. (2015)	Co- fermentation of hemicellulose and starch from barley straw	0.34	[51]
Thang & Kobayashi (2014)	Direct fermentation of native starches (uncooked process)	0.37	[52]
Qureshi et al. (2010)	The use of corn Stover and switch grass hydrolysates	0.37	[53]
Abd-Alla et al. 2015; Abd-Alla & Elsadek El-Enany (2012)	Spoilage date palm (phoenix dactyliferous l.) Fruits	0.39	[54,55]
Bellido et al. (2015)	Sugar beet pulp (SBP) with pre-treatment	0.44	[56]

residues such as straws (wheat and rice) and corn fibre are economically available, these materials must go through a pre-treatment and enzymatic hydrolysis steps in order to be suitable for fermentation. These processes produce inhibitors such as salts, furfural, hydroxyethyl furfural (HMF), acetic, ferulic, glucuronic, coumaric acids, and phenolic compounds [1]. Anaerobic bacteria, such as *clostridia* are capable of converting a wide range of carbon sources (e.g. glucose, galactose, cellobiose, mannose, xylose, and arabinose) to biofuels. The main aim of the pre-treatment is to improve the yield of sugars from biomass in the hydrolysis step. The pre-treatment breaks the lignin seal and removes most of the hemicellulose and lignin. A number of techniques such as acid, lime, steam explosion and ammonia pre-treatment can be used for this purpose [37,59–62]. For example, applying steam explosion combined with addition of $H_2SO_4/SO_2/CO_2$ is one of these ways for improving the enzymatic hydrolysis, which also decrease the production of inhibitory compounds. In addition, ammonia fibre explosion (AFEX) [63] and CO_2 explosion are other methods to increase the hydrolysis rate. Moreover, Ozone can be used to degrade lignin and hemicellulos [64,65]. Furthermore, acid hydrolysis using concentrated acids and diluted acids [66] have been in use for the pre-treatment of lignocellulosic materials for decades. There is also a biological pre-treatment which requires low energy and mild environmental conditions, but the hydrolysis rate is very low [67]. There are a number of bacteria strains that can be used for fermentation such as: *Clostridium, Cellulomonas, Bacillus, Thermomonospora, Ruminococcus, Bacteroides, Erwinia, Acetovibrio, Microbispora, and Streptomyces)* [68]. Genetic techniques have been used to clone the cellulose coding sequences into bacteria, yeasts, fungi, and plants to create new cellulose production systems, with possible improvements of enzyme production and activity, and also reduce the cost of production [69]. Qureshi et al. [70] reported that fermentation of fermentation of alkaline peroxide pre-treatment of wheat straw. The pre-treated of wheat straw hydrolysed using cellulolytic and xylanolytic enzymes by C. *Beijerinckii* P260 resulted in the production of 21.37 $g\,L^{-1}$ ABE yield and productivity of 0.3 $g\,L^{-1}\,h^{-1}$.

Same research group [53] also investigated in corn Stover hydrolysate with C. *Beijerinckii* P260 strain. The result presented ability to produce 26.27 $g\,L^{-1}$ ABE after inhibitor removal. They also reported that cultures resistant to inhibitors are more capable to produce butanol at high concentrations. This method may be another technique to improve the current process. A comparison of the use of different substrates (corn fibre, wheat straw) and different pre-treatment techniques (Dilute Sulfuric Acid, Alkaline Peroxide) suggests that a generation of inhibitors is substrate- and pre-treatment-specific. Nasib et al. [71] also produced ABE from wheat straw (WS) by *C. Beijerinckii* P260. Five different methods were investigated: pre-treatment, separate hydrolysis, without removing sediments, simultaneous hydrolysis and fermentation of WS without agitation, simultaneous hydrolysis and fermentation with additional sugar supplementation, and simultaneous hydrolysis. There are a number of pre-treatment techniques such as physical, chemical, physico-chemical, biological and combination pre-treatment that can be used to improve fermentation product Fig. 4 [61,62].

Table 3 shows comparative analysis of yield ($g\,g^{-1)}$ and productivity ($g\,L^{-1}\,h^{-1}$ in ABE production) in through anaerobic *Clostrial* fermentation in acid treated and enzyme assisted acid pre-treated. The summary of the Table 3 presents a significant improvement in productivity and ABE yield produced from a variety biomass. Different pre-treatment techniques were used.

2.4. Summary

Recent research has shown significant ABE yield improvements when using a combination of genetic engineering, pre-treatments and fermentation techniques. Continuing to use lignocellulose as raw material of fermentation and improve substrate utilisation together with enhancement of the development of genetic engineering strains and emerging pre-treatment technologies could make the ABE industry economically feasible. In addition, another strategy could also reduce the cost of ABE, by using a new technique of recovering ABE from the broth with less energy consumption.

Therefore, research should be employed in terms of the recovery and separating industry. Another way could decrease the cost of separation of ABE by utilising a low purity mixture with 5–10% water: each 10% of water removed from the broth contributes approximately 10% of the separation cost. The recovery cost consumes more than 40%

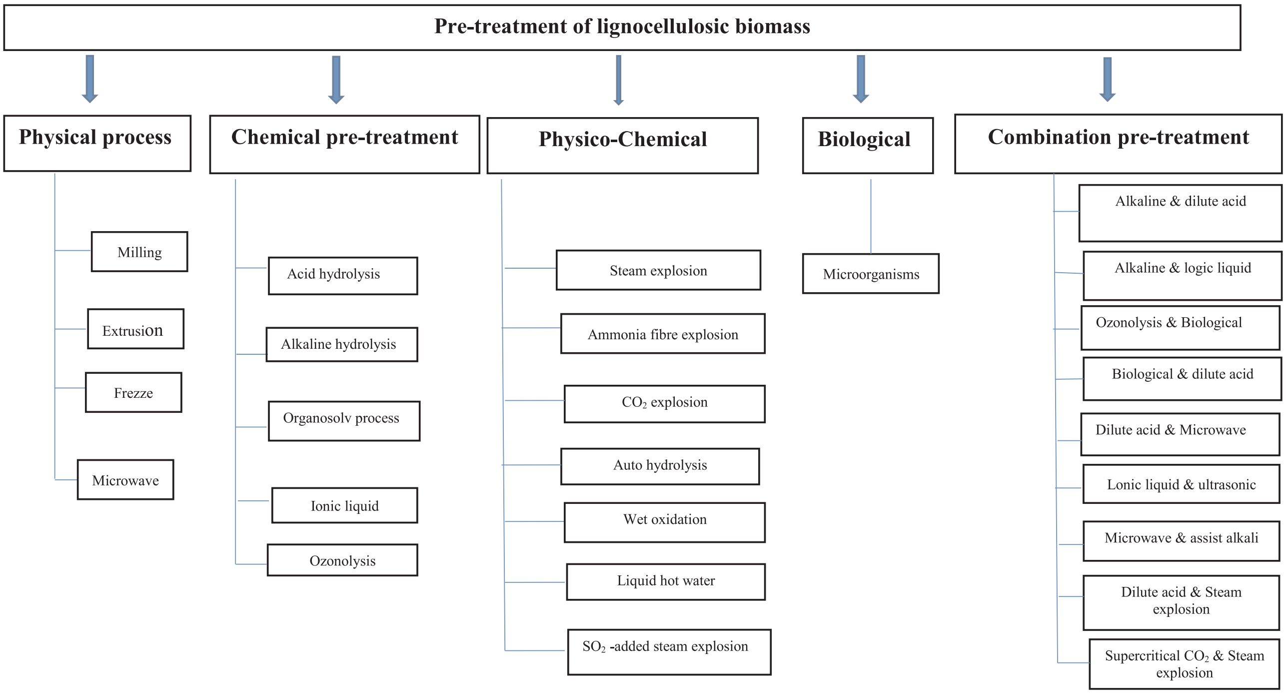


Fig. 4. Pre-treatment types used of lignocellulosic fermentation adapted from [61,62].

Table 3
Comparative analysis of yield (g $g^{-1)}$ and productivity (g L^{-1} h^{-1} in ABE production) used different anaerobic Clostrial fermentation through different pre-treated technique.

Author	Biomass type substrate	Strain	Retreatment	Yield g L^{-1} Before treatment.	Productivity (g L^{-1} $h^{-1)}$	Yield (g g^{-1})	Yield after treatment (g L^{-1})	Refs
Isar et al. (2013)	Lignoja cellulosic tropha Seed Cake	Clostridium Acetobutylicum	Acid	21.6	0.255	0.45	30	[43]
Li et al. (2014)	Gelatinized cassava starch	Clostridium acetobutylicum PW12	Atmospheric & room temperature plasma	9.3	0.28	0.31	N	[44]
Zhang et al. (2012)	Corncob Residue	Clostridium Beijerinckii NCIMB 8052	Ca $(OH)_2$ detoxification	16	0.33	0.32	19.9	[4]
Qureshi, Ezeji, et al. (2008)	Corn fibre	Clostridium Beijerinckii BA101	Acid & enzyme	9.3	0.1	0.35 to 0.39	16	[38]
Yang et al. (2015)	Barley straw		Xylanase & surfactants in enzymatic (acid-pre-treated)	0.093	N	0.135	10.8	[73]
Amiri & Karimi (2015)	Woody biomass	Clostridium Acetobutylicum	organosolv	5.5	N	0.1211	11.6	[74]
Moradi et al. (2013)	Rice straw	Clostridium acetobutylicum	Acid & Alkaline Treatment with NaOH	11	N	0.64, 0.63	20	[45]
Ranjan et al. (2013)	Rice straw	C. acetobutylicum NRRL B – 591	Ethanol organosolv pre-treatment (75% EtOH; 1% H_2SO_4 180 C; 30 min)	6	0.20	0.1239	10.5	[75]
Ranjan & Moholkar (2013)	Rice straw	C. Acetobutylicum MTCC 481	Dilute acid (1% H_2SO_4;60 C; 24 h and 121 C; 15 min)	1	0.017	0.0424	2.07	[3]
Gottumukkala et al. (2013)	Rice straw	Clostridium Sporogenes BE01	Acid (4% H_2SO_4; 121 C; 60 min)	20	0.050	0.532	53.2	[76]
Bellido et al. (2015)	Sugar beet pulp	Clostridium Beijerinckii	Autohydrolysis at pH 4	0.05	N	0.114	0.1432	[56]
Qureshi et al. (2010)	Corn Stover and switchgrass	Clostridium Beijerinckii P260	Ca $(OH)_2$	8.91	0.17–0.21	0.37	26.27	[53]
Huang W ei-cho (2004)	Corn	C.acetobutylicum via butyric acid	Via butyric acid Cell immobilization	8.5	4.6	0.53	14	[77]
Qureshi, Saha, et al. (2008)	Wheat straw	Clostridium beijerinckii P260	Alkaline peroxide pre-treatment of wheat straw. (dilute sulfuric acid, alkaline peroxide)	N	03–0.55	N	22.17	[70]
Ellis et al. (2012)	Waste water algae	Clostridium N1-4	xylanase and celluloenzymes Free and immobilized cells	0.73	0.102	N N	7.27 9.74	[78]
Kheyrandish et al. (2015)	Potato waste starch	Clostridium acetobutylicum		9.9	0.33	N	60	[49]

of production budgets [72]. In conclusion, there are improvements in bioreactor performance, development of genetically engineered yeast strains and more efficient pre-treatment technologies, which all contribute to the economy and feasibility of ABE production from lignocellulose.

3. Applications of alcohol as an additive fuel

3.1. Bio-alcohol application in internal combustion engines

Alcohols have been widely used in internal combustion (IC) engines because of a number of benefits: (1) high oxygen content, high stoichiometric air–fuel ratio and high hydrogen–carbon ratio. These benefits result in completing the combustion and emitting fewer emissions [79]; (2) laminar flame propagation speed is higher, which may lead to earlier completion of the combustion process resulting in improved thermal efficiency of the engine [80]; and (3) ignition propensity (i.e., knock resistance and octane rating) of alcohols. This benefit is the most attractive behaviour for IC applications, especially of SI engines. A higher octane rating correlates with a lower propensity for ignition and allows the SI engines to operate at a higher compression ratio without knocking [81]. Therefore, these benefits of alcohol, especially (ethanol and butanol), have encouraged researchers to use it as an additive blend with gasoline [82–86] and diesel [7,87–102].

The use of ethanol as an alternative fuel for gasoline has attracted considerable interest, mostly in the US (ethanol produces from corn), Brazil (ethanol produces from sugar cane), and Sweden as E85 (15% gasoline-85% ethanol) has been commercially used before 20 years ago.

Ethanol is also used as an additive fuel up to 10% in gasoline (E10) in a number of markets such as Australia [85]. There are a number of advantages of blending ethanol in gasoline: (1) decreases CO and NO_x emissions; (2) it is a renewable fuel; (3) decreases the pollution; and (4) its high octane number leads to be a good spark ignition engine's fuel.

The use of ethanol as an additive blend of diesel has been experimentally investigated [86–122]. These studies support the claim that ethanol has a number of obstacles as an additive blend of diesel: (1) limited miscibility in diesel fuel and phase separation, especially at low temperatures [96]; (2) unsuitable fuel properties for diesel engine design such as a lower cetane number, lubricity and heating value [58].

However, there are some difficulties with blending ethanol with either gasoline or diesel: (1) ethanol liquid fuel safety especially in the fuel tank are usually combustible at ambient temperatures, causing risk of an explosion, particularly during refuelling [123]; (2) the corrosive nature of ethanol, so it is not recommended for use with components made from brass, copper and aluminium. Another consequence of the corrosive nature of ethanol is that rubber is also affected by an ethanol blend because of a physical reaction which leads to a jam in the fuel supply pipe [124]; and (3) production methods for first generation biofuel (edible crops used to produce bioethanol) may lead to shortages of food and result in increased food prices [125].

Therefore, some researchers have focused on the use of butanol as a suitable blend for CI engines [5,58,105,117,118,123,126–149] and SI engines [150–161]. Butanol presents a number of advantages and one drawback compared with ethanol: it has a higher cetane number (CN) (25 vs 8), higher kinematic viscosity (2.63 mm^2/s vs 1.08 mm^2/s) and higher heating value (33,100 MJ/kg vs 26.8 MJ/kg). These benefits can be utilised to improve the fuel properties of blends, improve engine performance and reduce emission levels. These benefits can contribute to providing power similar to transportation fuel while producing fewer emissions [143,162–164]. However, the cost of butanol production is the main issue limiting its use as a fuel in internal combustion (IC) engines. Butanol can be produced through either ABE or BA fermentation processes [20,24,48]. The ABE or BA (the intermediate outcome during the production of butanol) mixture can be further purified to produce pure acetone, butanol, and ethanol. Hence, ABE or BA has been proposed as alternative alcohol additives for conventional fuel to decrease production costs. The typical production ratios are ABE (3:6:1) and BA (2.9:1) with varying concentrations [24,53]. Fig. 5 shows a snapshot of the number of papers and reports that were published during the last 9 years. These publications investigated three types of alcohol (ethanol, butanol and ABE) as an additive fuel for diesel and gasoline engines. There is a deficiency in the number of studies regarding ABE in internal combustion (IC) engines; therefore, several investigations are needed to cover different operating conditions to obtain enough data for more complete understanding.

3.2. Ethanol in internal combustion engines

Many researchers have comprehensively investigated ethanol blended with diesel in CI engines as well as an additive blend with gasoline in SI engines. The experiments were carried out in different blend ratios and different operating engine conditions.

3.2.1. Ethanol properties

Ethanol is a two-carbon alcohol with six hydrogen atoms (C_2H_6O) and has a low cetane number (8), low heating value (26.8 MJ/kg) and low viscosity (1.08 mm^2/s) at 40 °C. Fig. 6 shows ethanol atoms. Table 4 shows the properties of diesel, gasoline, ethanol, acetone and butanol.

Furthermore, the stability of any blend is an important factor in fuel properties. The most significant issue of using ethanol with diesel is solubility and miscibility. In order to stabilise ethanol-diesel blends, two additives can be added: surfactants (emulsifiers) or co-solvents to assist a stable blend form. Therefore, the use of biodiesel is an important method to stabilise ethanol in diesel [107,112]. There is no separation issue resulting from adding ethanol to gasoline at any blend ratios, which means the mixture is stable. Pidol et al. [112] studied the effect of ethanol, biodiesel, and diesel on fuel properties such as blend stability. The blends were prepared by a two-step procedure: first, ethanol and Fatty Acid Methyl Esters (FAME) were blended together, and second, diesel fuel was added. This process produced more stable blends. Moreover, the addition of multicomponent biodiesel, Fatty Acid Methyl and Ethyl Ester (rapeseed oil methyl and ethyl ester) to ethanol-diesel blends was a good way to stabilise ethanol in diesel. [165].

Barabás et al. [107] investigated 27 mixture samples of ethanol, biodiesel and diesel in different ratios. The experiments showed that only seven samples were suitable in terms of miscibility and stability and two samples (B10D85E5 and B25D70E5) could successfully replace diesel.

3.2.2. Combustion characteristics of ethanol

Combustion characteristics of ethanol as a fuel and as a blend have been widely investigated. Veloo et al. [170] experimentally measured laminar flame speeds and extinction strain rates of premixed methanol, ethanol, and n-butanol flames in a counter-flow configuration at atmospheric pressure and elevated unburned mixture temperatures. Results showed that the laminar flame speeds of ethanol/air and n-butanol/air are similar. They also found that under fuel-rich conditions, methanol/air laminar flame speed are significantly higher than ethanol/air and n-butanol/air flame speeds.

Li et al. [171] studied the laminar flame behaviours of ethanol-air, n-butanol-air and n-pentanol-air mixtures at 393 K and 0.1 MPa. According to the comparison with previous studies by those authors, for lean mixtures it was found that the laminar flame speed of ethanol is the fastest. The laminar speeds of these three alcohols showed very similar values for rich mixtures. They also found that the effective Lewis number of ethanol is lower than that of n-butanol. The hydrodynamic instability of n-butanol is higher than that of ethanol, so is enhanced with the increase in carbon number. The flame thicknesses were very similar for the three fuels.

Another study by Li et al. [172] also studied the laminar combustion characteristics of isooctane and C1-C2 primary alcohols (methanol, ethanol, n-propanol, n-butanol and n pentanol). The test was carried out in a constant volume chamber at various equivalence ratios and blend ratios of alcohol. Their results indicated that (1) laminar flame speeds of isooctane-alcohols blends was increased monotonously as a result of increasing volume blend ratios of alcohol, (2) methanol addition was identified to be the most effective in enhancing flame speed comparing to other alcohols. The addition of ethanol results in an approximately equivalent laminar flame speed enhancement rate as those of n- propanol, n-butanol and n-pentanol at ratios of 0.8 and 1.5, and a higher rate at 1.0 and 1.2. The laminar flame speed increases with the mass content of oxygen in the fuel blends.

Beeckmann et al. [173] also studied the laminar burning velocities of methanol, ethanol, n-propanol, n-butanol and ethanol in a spherical combustion vessel at an unburnt temperature of 373 K and a pressure of 10 bars. Beekmann also compared with the results available in published literature to those of numerical simulation data from published chemical mechanisms. A sensitivity analysis suggests further investigation of the pressure dependence for the fuel-specific reactions with hydrogen and hydroxyl radicals would be worthwhile.

Mohamed [174] measured the burning velocities of mixtures of air with ethanol and butanol by measuring flame speed and flame temperature using a tube method. The test was carried out using different fuel-air ratios (0.7 ≤ ϕ ≤ 1.4). The experimental data showed that the maximum values of burning velocity, flame speed and flame temperature occurred at ϕ =1.1. Table 5 compares the maximum values of flame speed, flame temperature and burning velocity of alcohols and conventional fuel. It can be seen from Table 5 that butanol had a higher burning velocity while acetone showed a lower burning velocity due to the impact of its chemical properties.

3.2.3. Ethanol blend tested in CI engines

Blending ethanol with diesel fuel has several issues in terms of performance and emission levels. A number of studies have examined the effect of ethanol on thermal efficiency, brake power, fuel consumption and emission levels. Some research [102,108,113,114] obtained different results in terms of performance and emission levels. Most of this research agreed that ethanol causes an increase in fuel consumption (BSFC) and a decrease in the efficiency of the diesel engines. Chen et al. [108] showed that ethanol could decrease some types of emissions such as smoke and PM because high oxygen content helps to complete the combustion. When vegetable methyl ester was added to

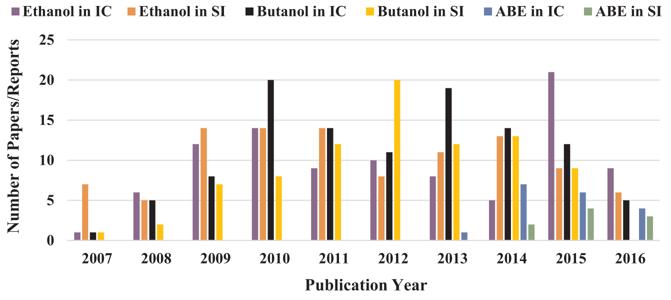
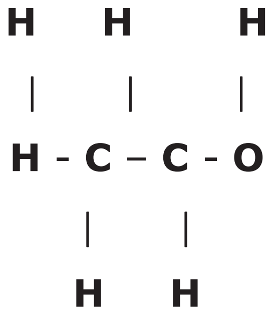


Fig. 5. Number of published papers/reports on CI engines and SI engines with ethanol-diesel blend ethanol-gasoline blend, butanol-diesel blend or butanol-gasoline blend and ABE-diesel blend or ABE-gasoline blend during the last 9 years.



$$\begin{array}{ccccccc} H & & H & & H \\ | & & | & & | \\ H & - & C & - & C & - & O \\ & & | & & | \\ & & H & & H \end{array}$$

Fig. 6. Ethanol molecular structure.

Table 4
Properties of alcohols and conventional fossil fuels [166–169].

Properties	Diesel	Gasoline	Ethanol	Butanol	Acetone
Chemical formula	C_{12}–C_{25}	C_4-C_{12}	C_2H_5OH	C_4H_9OH	C_3H_5OH
Cetane number	40	8	8	25	
Oxygen content (wt%)		0–4	34.78	21.62	27.59
Density at 288 K (g/mL)	0.82–0.86	0.765	0.795	0.813	0.791
Lower heating value (MJ/kg)	42.7	43.5	26.8	33.1	29.6
Stoichiometric ratio	14.3	14.6	9.02	11.21	9.54
Viscosity at 413 K (mm^2/s)	1.9–4.1	0.494	1.08	2.63	0.35
Boiling point (°C)	200–400	38–204	78	117	55.5–57.5
Ignition temp (°C)	230	300	434	385	565
Latent heat @ (25 °C) (kJ/kg)	270	380–500	904	582	518

Table 5
Maximum values of flame speed, flame temperature and burning velocity (at 1 atm, 325 K) for butanol and ethanol fuels [174,175], acetone [176] and ABE [177].

Fuel	Sf (cm/s)	T_b (K)	S_u (cm/s)	Ref.
Ethanol	360	2310	48.9	[174]
Butanol	350	2340	46	[174]
Acetone	NA	NA	35	[176]
Gasoline	350	2330	46	[175]
Diesel	NA	NA	33	[98]
ABE	NA	NA	37	[178]

NA: not available.

ethanol-diesel, the result showed that decrease in engine torque by 6–7% for every 10% (by volume) ethanol added to the diesel fuel. NO_x emissions reported in this study were slightly higher than the NO_x emissions of diesel fuel. The quantity of energy and emission levels produced during the use of ethanol depended on the volumetric ratios of ethanol added to the blend. Subbaiah et al. [102] found that BTE increased because of blending 15% ethanol with rice bran oil (biodiesel) and diesel. CO, smoke and the exhaust gas temperature also reduced significantly with higher ethanol ratios due to decreased combustion temperature. However, HC, NO_x and CO_2 emissions increased with the increase of ethanol ratios. Cheenkachorn and Fungtammasan [114] reported that there is a significant reduction in emission levels, especially PM and CO compared to regular diesel. Blending 0.25% (vol.) hydrous ethanol, 4.75% anhydrous ethanol, and 11% biodiesel with 84% diesel can reduce the average PM level to be 39% lower for the ethanol-diesel-biodiesel blend than that of regular diesel; also CO emissions are significantly lower than regular diesel, but NO_x emissions change from case to case. Furthermore, Hulwan et al. [113] investigated different blend ratios from ethanol, biodiesel and diesel in CI engines. BSFC increased because of increased ethanol in the blend. However, BTE and smoke opacity reduced by 21%. NOx emission level variation depended on operating conditions. CO emissions drastically increased at low loads. There was a significant difference in exhaust gas temperature. Moreover, the addition of ethanol to diesel increases ignition delay and combustion noise. To reduce combustion noise, CN improver can be added to the fuel.

A number of previous studies tested the impact of ethanol-diesel blends with adding CN improver on CI engine [179–181]. Park et al. [182] studied the spray and combustion characteristics of a commercial 4-cylinder diesel engine, fuelled with ethanol-diesel blend. Spray tip penetration of ethanol-diesel was shorter comparing with pure diesel fuel. The large reduction rate in tip penetration was occurring due to decrease in blend density. However, larger spray cone angles achieved as result of adding ethanol comparing with pure diesel fuel. In addition, advancing the injection timing led to an increase in combustion pressure. No_x emission was decreased when the amount of ethanol in the blend was increased. In contrast CO and HC emissions were increased with the increase in ethanol blending ratio.

Furthermore, several investigators have studied the impact of ethanol fumigation on engine performance and emissions [183,184]. Alcohol fumigation is additional technique that can be used to improve the quality of air-fuel mixing of CI engine. In this technique, premixed alcohol vaporized and injected with intake air while the diesel fuel is injected directly into the cylinder as in a normal diesel engine. Fumigation needs minor modifications to the engine. Alcohol can be injected into the air intake using the low-pressure fuel injector system. The result of ethanol fumigation caused significant reductions in smoke, PM and NO_x emissions. However, HC and CO emissions were increased. BTE was not clearly affected.

To summarise, stable blends of ethanol in diesel require extra cost such as adding surfactant or engine modification such as fumigation. Experimental studies showed the drawbacks of blending ethanol with diesel in diesel engines in relation to increased BSFC and reduced BTE of diesel engines. The emissions results illustrate that: CO emissions are significantly lower than with regular diesel, but NO_x emissions change from case to case. Table 6 presents different results for engine performance and emissions when using the additive ethanol to blend with gasoline or diesel fuel.

3.2.4. Ethanol blend tested in SI engines

Ethanol is commonly used in SI engines due to advantages of ethanol's properties such as density and octane number, which makes it a suitable for blending in SI engines. It also decreases knock characteristics, which allows the use of higher compression ratios and resultant higher thermal efficiencies [185–194]. Moreover, ethanol has some advantages over gasoline, such as the reduction of CO, and unburned HC emission levels [82,84,187,195]. In addition, the flame of the alcohol is colourless in the natural burning process which leads to cleaner combustion [196]. Recently, ethanol has been used in SI engines with gasoline at low concentrations (5–15%) vol. either without any engine modification or requiring minor changes in the engine structure [197]. Furthermore, pure ethanol or 85% vol. blended with 15% gasoline can be used in spark-ignition engines following some modifications to the SI engines [198–200]. However, some companies built engines suitable for ethanol fuel. Indeed, Henry Ford's model T was built to run on pure ethanol and gasoline [201]. A number of studies [86,202] experimentally investigated the effect of ethanol-gasoline mixture on exhaust emissions with ratio 5%, 10%, and 15% vol. Ethanol blending reduces CO and UHC concentration in the exhaust gases by about 45% and 40%, respectively, while another study showed that CO emissions decreased by 35% [86]. NO_x and CO_2 concentrations in the exhaust gases increased by about 16.18% and 7.5% respectively [203]. However, another research reported that the biggest advantage of adding ethanol is NO_x reduction, which is reduced by 83% when it is used in high percentages of ethanol (15%) and on average 38% for other cases. Research has been undertaken [84,203] that tested different ratios of ethanol E10, E15, E20 and gasoline of direct injection SI engine cars. The authors reported that there is a significant reduction of

Table 6
Summary of some research into additive ethanol as blend for SI and CI engines.

Author	Alcohol	Reference fuel	Engine tested	Ethanol %	Test results	Year
Shahad & Wabdan [202]	Ethanol	Gasoline	Single-cylinder	5, 10 & 15	↓CO & ↓NO_x & ↑CO_2 and ↑UHC	2015
Türköz et al. [187]	Ethanol	Gasoline	4-stroke, 4-cylinder	85	↑NO_x, ↑CO & CO_2 are not being affected. ↑ignition delay timing leaded to lesser combustion resulting in ↑ UHC & ↑SFC	2014
Karavalakis et al. [203]	Ethanol	Gasoline	DI engine	10, 15 & 20	Particle number ↓ when E10. Black carbon showed significant ↓ with E15 & E20	2014
Lapuerta et al. [119]	Ethanol	Diesel	4-cylinder, 4- stroke, EGR, turbo & DI	10 & 15	slight ↑BTE ↓ CO & ↓NO*x* emissions	2008
Bielaczyc et al. [84]	Ethanol	Gasoline	4-stroke & 4-cylinder	10, 25, 50 & 85	Particles (diameter 23 nm). Increases in PM or PN emissions in response to increasing blend ethanol content are rather un likely to be statistically significant.	2014
Cheenkachorn & Fungtammasan [114]	Ethanol	Diesel	4-cylinder, 2004 Isuzu (2.5 L) & DI	0.25 hydrous E & 4.75 anhydrous E	↓CO, ↑BSFC & ↓PM, ↓BP No significant difference CO_2, NO_x & SFC	2010
Hulwan & Joshi [113]	Ethanol	Diesel	Multi-cylinder & DI	20, 30 & 40	↑CO, ↑BSFC, ↑BTE & ↓ smoke opacity by 21% at a high load. NO*x* variation depended on operating & significant difference in exhaust gas temperature.	2011
Park et al. [182]	Ethanol	Diesel	4-cylinder	20	↓NO_x,↑ CO & ↑HC with ↑ ethanol ratio. Shorter S, larger spray cone angles with ↑ ethanol ratio.	2011
Chen Hu et al. [108]	Ethanol	Diesel	4-stroke, 4-Cylinder Cummins	10, 20 & 30	↓ T 6–7% for every 10% with ethanol added, ↑BSFC, ↓Smoke and ↓PM, PM reduction is less significant than smoke reduction.	2008
Subbaiah et al. [102]	Ethanol	Diesel	4-stroke, single-cylinder & DI	5, 10 & 15	BTE increased CO, smoke & exhaust gas temperature also ↓, HC, NO_x and CO_2 emissions ↑ significantly	2010

Note:↑, increase & ↓, decrease.

particle number emissions as a consequence of higher ethanol than E10. Black carbon emission was also significantly decreased with E15 and E20. Hsieh et al. [82] investigated the impact of ethanol–gasoline with ratios 0%, 5%, 10%, 20% and 30% vol. on commercial SI engines. Increasing the ethanol content in the blend causes a decrease in the heating value of the mixture while the octane number is increased. The torque output and SFC were slightly increased; CO and HC emission levels were decreased dramatically as a result of the leaning effect caused by the ethanol addition; CO_2 emission levels were also increased due to improving combustion. NO_x emission levels depended on the operating condition of the engine rather than ethanol content. Graham et al. [199] evaluated the effect of blend ethanol-gasolines with ratio E10, E20 and E85 together with statistical analysis. There is a significant decrease in the CO emission levels by 16% as a result of the use of E10 while NO_x and CO_2 emission levels showed no significant changes. E85 produces a significant decrease in emission levels of NO_x (by 45%) while CO and CO_2 emission levels showed no significant changes. Other studies [196,197,199] investigated the effect of 85% ethanol emission levels tested in SI engines. The use of E85 resulted in a significant decrease in NO_x emission levels and no notable change in CO emission levels. Higher levels of HC were caused by E85 compared to E0 during most of the engine operating conditions. However, CO emission level was marginally decreased as a result of adding E85. In addition, E85 had a slightly faster burning velocity rate than E0 [196]. Türköz et al. [187] also tested the effect of E85 on SI engine under various ignition timings. The author reported that advanced ignition timing resulted in an increase in NO_x emission level, while CO and CO_2 were not affected. Increasing the ignition delay timing led to diminished combustion resulting in higher UHC and SFC.

3.3. *Butanol in internal combustion engines*

Many studies have investigated butanol as an additive for blending with diesel in CI engines and gasoline in SI engines. Experiments were carried out for different blend ratios and changing operating conditions such as the use of turbochargers [141] and exhaust gas recirculation (EGR)

3.3.1. *Butanol properties*

Butanol contains four carbon atoms and ten hydrogen (C_4H_9OH) in four isomers: normal-butanol ($CH_3CH_2CH_2CH_2OH$), secondary butanol ($CH_3CH_2CHOHCH_3$), isobutanol ($(CH_3)_2CH_2CHOH$) and tert-butanol ($(CH_3)_3$ COH). All butanol types contain about the same energy [18]. Butanol is far less corrosive than ethanol and easier to blend with gasoline and diesel. Butanol contains 22% oxygen, making it cleaner burning than ethanol [20]. A number of research projects [18,130,141] have also reported that when operated in IC engines it yields carbon dioxide (CO_2) and less (CO), making it a more environmentally friendly alcohol (Fig. 7).

The main advantage of blending butanol with diesel and gasoline is miscibility and stability at any ratio. Laza et al. [5] studied the effect higher alcohol blends (1-propanol, 2-propanol, isobutane, n-butanol and sec-butanol) and of rapeseed oil (RSO) on blend stability.

The blends were prepared in the proportion of 10% and 20% by volume of alcohol. The main fuel properties such as stability, density, heating value, viscosity, and cetane number (CN) of the blend were measured using Standard Methods. The results indicated that firstly, the blends were stable at all volume ratios of butanol. Secondly, the viscosity, cold filter plugging point (CFPP) and heating value of the blends increased with a decrease of alcohols ratio in the blends.

Atmanli et al. [132] investigated different types of vegetable oil, crude canola (Cn), soybean (Sb), sun-flower (SF), corn (Cr), olive (Ol), and hazelnut oil (Hn) with diesel by using normal butanol (nB) as solvent. The fuel in six different ternary blends was prepared via the splash blending method. The ternary blend was stored at ambient temperature for long-term stability for about 60 days. The test was

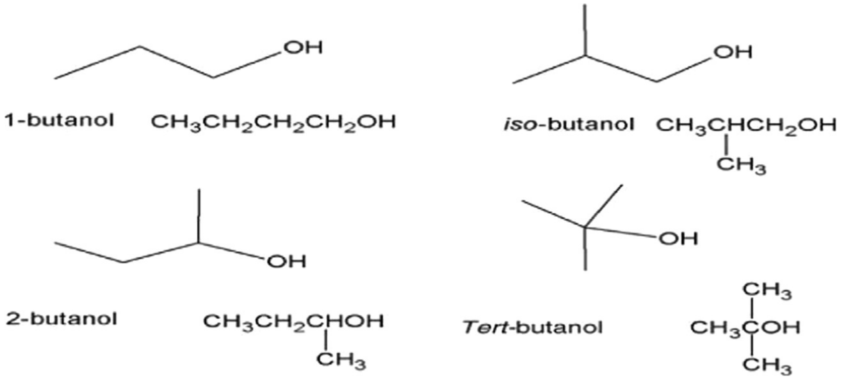


Fig. 7. Butanol isomer adapted from [1].

presented without any phase separations in the ternary blends.

3.3.2. Combustion characteristics of butanol

In fundamental combustion experiments of butanol isomers such as the laminar burning velocity, flame speed, flame thickness and ignition delay time were measured; and the intermediate species formed in premixed combustion or diffusion combustion were studied at different operating conditions [204,205]. Different chemical kinetic models of butanol isomers were developed using these experimental works as validation data. These reaction models can provide a better understanding of the butanol isomers' combustion characteristics. A number of studies investigated the combustion characteristics of the butanol isomers (n-butanol, sec-butanol, isobutanol, and tert-butanol) through different operating conditions such as initial temperature, initial pressure, equivalence ratios and blend ratio using a variety of measuring techniques.

Gu et al. [206] measured the laminar burning velocity and Markstein lengths of n-butanol-air premixed mixtures over a wide range of ϕ at initial temperatures of 413 K, 434 K and 473 K and initial pressures of 0.1 and 0.25 MPa using high-speed Schlieren photography and outwardly propagating flames. They also studied the effect of laminar flame thickness, thermal expansion ratio and flame Lewis number on flame stability. They found that: (1) laminar burning velocity and flame propagation speeds decrease as a result of increased initial pressure; (2) the laminar velocity is increased as a result of increased initial temperature; (3) n-butanol-air premixed flames showed the maximum value of laminar burning velocity at $\phi = 1.3$; (4) Markstein length increased with increased initial pressure and decreases with the increase of ϕ; (5) flame thickness is decreased remarkably as a result of increased initial pressure; (6) thermal diffusive instability of the flame front is increased as a result of increased initial pressure and this leads to increased initial temperature.

Another study by Gu et al. [207] also investigated the laminar burning velocities and flame instabilities of the different butanol isomers premixed with air using a spherically expanding flame with central ignition at an initial temperature of 428 K and initial pressures of 0.10 MPa, 0.25 MPa, 0.50 MPa and 0.75 MPa. The authors obtained unstretched laminar burning velocity, Lewis number, adiabatic flame

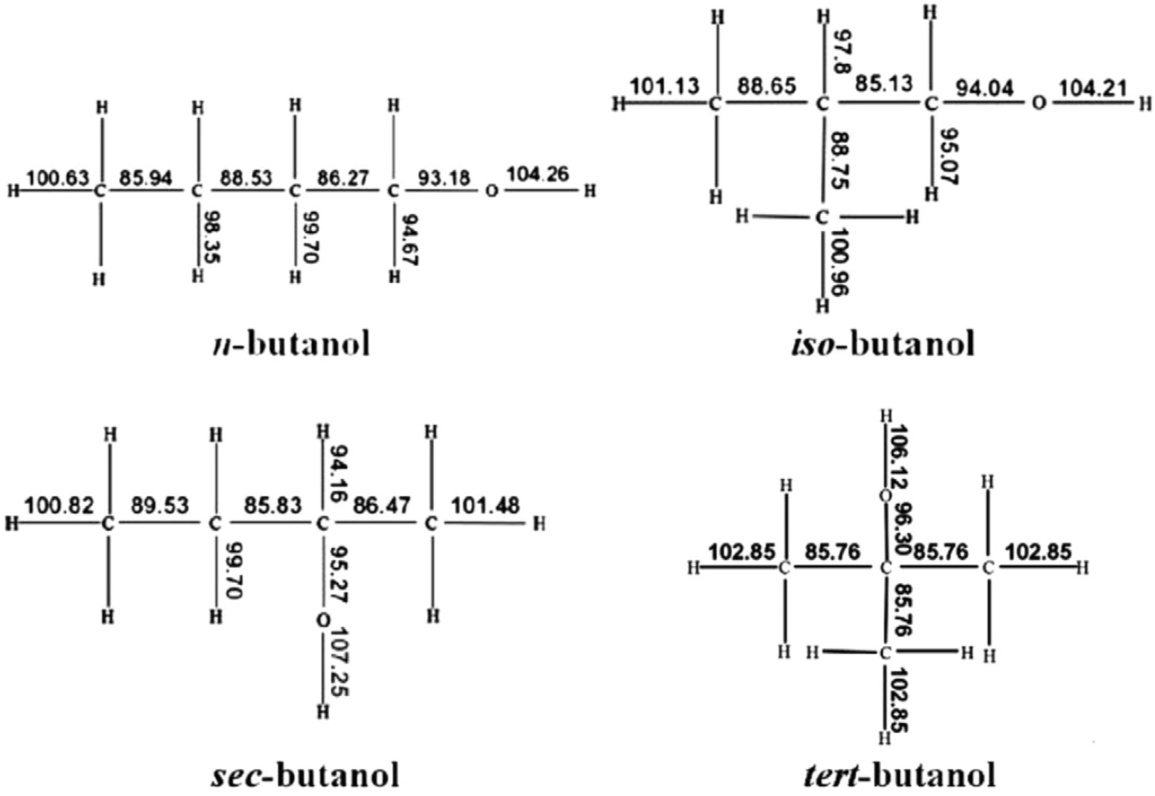


Fig. 8. Dissociation bond energies of butanol isomers [207].

temperature, Markstein length, critical flame radius and Peclet number over a wide range of equivalence ratios (ϕ). Of these, the following properties were not significantly different for the various isomers: adiabatic flame temperatures of the butanol isomers are the same value; flame radius is not affected via cellular structures of butanol isomers; flame instability has been little affected by the molecular structure of the butanol isomers–air mixtures; instability of flame is mainly affected by both diffusive-thermal instabilities and hydrodynamic basis. However, laminar burning velocities provide a clear difference among the butanol isomers. The impact of molecular structure on laminar burning velocity of butanol isomers was also investigated from the aspect of C–H bond dissociation energy. The data results showed that: n-butanol has the maximum laminar burning velocities, while tert-butanol has the lowest value, with the values significantly affected by the functional groups. The -CH_3 branch leads to decreased laminar burning velocity. If the OH group is attached to the inner carbon atoms, lower laminar burning velocity is observed compared to when the group is attached to the terminal carbon atoms. Inner C–H bonds have smaller bond energies than terminal C–H bonds. The H-abstraction reaction is slower for high bond energy value, which leads to a low overall reaction rate. N-butanol has the highest laminar burning velocity because it has the most inner C–H bonds. Tert-Butanol, with no inner C–H bonds, has the lowest laminar burning velocity. The laminar burning velocity of sec-butanol is higher than that of isobutanol. Fig. 8 showed dissociation bond energies of butanol isomers.

Wu and Law [208] measured the laminar flame speeds for the four butanol isomers at pressures from 1 to 5 atm. They found that n-butanol presents the highest flame speeds while tert-butanol showed the lowest at all pressures. Some computational models showed satisfactory agreements, while other models did not. The authors found that the primary reason for the lowered flame speed of sec-butanol, isobutanol and tert-butanol is that they crack into more branched intermediate species which are relatively stable. This indicates that the general rule that fuel branching reduces flame speed for hydrocarbons can also be applied to alcohols, and that the fundamental reason for this case is that, in alcohols, the O–C bond has a similar bond energy to the C–C bond while O–H has similar bond energy to the C–H bond.

Gu et al. [209] experimentally and numerically studied laminar burning characteristics of premixed diluted n-butanol air. The experiment was carried out using spherically expanding flames at different dilution ratios of nitrogen at an initial pressure of 0.1 MPa and a temperature of 428 K. Experimental and simulation work demonstrated that the laminar flame speed of n-butanol/air mixtures is decreased as a result of the increase of the dilution ratio of nitrogen due to the decrease of the adiabatic flame temperature of the mixtures. Data showed that the flame tends to stabilise with nitrogen dilution for the n-butanol air mixture when ϕ is less than 1.4. However, the flame tends to become unstable when the mixtures are diluted with nitrogen when ϕ is at least 1.4. The measured laminar flame speeds are in good agreement with the computed laminar flame speeds at different nitrogen dilution ratios. Results also showed a linear relation between the normalised laminar flame speed and the nitrogen dilution ratio regardless of equivalence ratios. When the kinetics were analysed, the H and OH radicals were found to play a major role in laminar flame speeds.

Sarathy et al. [210] studied the combustion characteristics of n-butanol blended with gasoline or diesel to produce alternative fuels. The authors reported new experimental data for n-butanol in three experimental configurations. The results are focused on the laminar burning velocity profiles in a jet stirred reactor (JSR) under atmospheric conditions and a range of equivalence ratios. The laminar flame speed was obtained in an n-butanol premixed laminar flame as well as species concentration profiles for n-butanol in an opposed-flow diffusion flame. The experimental results showed that the laminar burning velocity had a maximum between $\phi = 0.8$ and 1.1, which corresponds to a maximum burning velocity of 47.7 cm/s, and then decreased at higher equivalence ratios (ϕ). The proposed model verified by the JSR and opposed-flow diffusion flame indicated that H-abstraction is the major pathway for n-butanol consumption followed by β-scission of the resulting fuel radicals.

Pan et al. [211] studied the ignition delay times of isobutanol with a fuel ratio of 0.1–0.5% under a temperature range of 900 −1700 K and at pressures of 1–1.2 atm and equivalence ratios of 0.5–2.0. Ignition delay results were compared with previous experimental results under same operating conditions and also compared with n-butanol, which was found to have shorter ignition delay times. However, the global activation energy of isobutanol is slightly smaller than that of n-butanol.

Zhang et al. [212] studied the ignition delay time of an n-heptane / n-butanol mixture with different ratios diluted with argon using reflected shock waves within the temperature range of 1200–1500 K, at pressures of 2 and 10 atm and equivalence ratios of 0.5 and 1. By studying the chemical structure of n-butanol, it can be found that only a very limited part of n-butanol participates in the low temperature branching because of the OH group impact, leading to an increase in ignition delay time. Ignition delay time was increased linearly with decreased n-butanol blend ratios at high temperatures, while it increased nonlinearly with increased n-butanol blend ratios at low temperatures. The authors also found that pure n-butanol has the longest ignition delay period. They also found that most of the n-butanol undergoes H-abstraction by OH radicals from α-carbon position to form α-hydroxybutyl at low temperatures. This results in a reaction with oxygen to form stable butyraldehyde, leading to an increased ignition delay time.

Another study by Zhang et al. [213] studied ignition delay times of n-butanol/oxygen diluted with argon by measuring behind reflected shock waves for temperatures of 1200 − 1650 K, pressures of 2–10 atm and equivalence ratios of 0.5, 1 and 2. The authors modified and developed a kinetic model for oxidation of n-butanol at high temperatures by adding some key reactions. A new model showed good prediction of the measured data under all measured conditions. Investigation of a reaction pathway indicated that H-abstraction reactions have significant impact on the n-butanol consumption, although unimolecular decomposition reactions become a more important factor with temperature increments.

Black et al. [214] studied auto ignition delay time of bio-butanol at equivalence ratios of 0.5, 1 and 2 at reflected shock pressures of 1, 2.6 and 8 atm in the temperature range of 1100–1800 K. Formation enthalpies and bond dissociation energies were determined for each alcohol bond. A detailed chemical kinetics model was developed and utilised to simulate butanol ignitions. The model was built and tested against measurements in a jet stirred reactor with good agreement.

Weber et al. [215] also experimentally studied the autoignition delay time of butanol. A heated rapid compression machine was used at high pressures ranging between 15 and 30 bars in the temperature range of 675– 925 K and for equivalence ratios of 0.5, 1, and 2. They found that the ignition delay time decreases continually as a result of increased temperature. A non-linear fit to the experimental data is performed and the reactivity, in terms of the inverse of ignition delay, shows nearly second-order dependence on the initial oxygen mole fraction and slightly greater than first-order dependence on initial fuel mole fraction and compressed pressure. The authors also compared experimental measurement of ignition delay time to simulations using several reaction mechanisms published in previous studies, but no satisfactory correlations were obtained.

Moss et al. [216] studied the oxidation of the four isomers of butanol (n-butanol, sec-butanol, isobutanol and tert-butanol) at high temperatures ranging from approximately 1200 K to 1800 K and pressures from 1 to 4 bars in a shock tube. They also developed a kinetic mechanism for the description of their high-temperature oxidation. This mechanism provided a good correlation with the experiments in terms of reactivity of the four isomers. Some mechanisms still remain unclear, but it concluded that tert-butanol and sec-butanol are less reactive.

3.3.3. Butanol blend tested in CI engines

Engine performance and emission levels resulting from operating butanol and diesel in CI engines have been extensively investigated. These studies revealed different results due to the different blend ratios and operating conditions [130,136].

A number of studies [105,132,139,143,217] have revealed an increase in BSFC when adding butanol to the blend of n-butanol/diesel fuel because of the lower heat content of butanol compared with conventional fuel. BTE was slightly increased as a consequence of adding the butanol [143]. Oxygen and cetane number can affect BTE, enhance in BTE can be related to the enhanced oxygen content and/or lowed cetane number, oxygen aids improvement in combustion. While the lower cetane number causes a longer ignition delay, leading to a wider ranging fraction of fuel burned in the premixed mode. Furthermore, burning speed of fuels has an important influence on BTE [96]. Higher laminar flame speed leads to higher efficiency. Butanol (C_4H_9OH) is a higher chain alcohol, which gives it a higher burning velocity [218]

Laminar burning velocity is 33 cm/s for diesel fuel [96] and 45 cm/s for butanol. Because of these factors, the variety of n-butanol content in the fuel blends elevates BTE.

Emission levels produced from blending butanol and biodiesel in diesel engines presented varying results for CO, CO_2, NO and HC. Some studies [105,130,132] showed a slight increase in CO_2 and a significant decrease in CO because of adding butanol. The fuel air mixing process was enhanced, especially in the rich region of the cylinder, by providing more oxygen because of the high oxygen content of the blends [105,117,130,140,141]. Research [117,130,140] has revealed that butanol could contribute to a decrease in NO_x level due to a decrease in the temperature of combustion. However, some research found a slight increase in NO and HC emissions levels when compared to those of diesel fuel when butanol was blended above 20% [105,140,141,143]. To conclude, butanol has many more advantages than ethanol with biodiesel or with diesel, regarding blend stability, engine performance and reduction in emissions.

Table 7 presents different results in terms of engine performance and emissions for butanol as a blend for diesel fuel.

3.3.4. Butanol blend tested in SI engines

Butanol is a high alcohol type C_4H_9OH and it has a better blend property compared with ethanol as an additive blend for gasoline in SI engines. This because it is less corrosive to aluminium or polymer components in the fuel system and has the ability to blend with gasoline at a high ratio without vehicle modification. Therefore, butanol has been widely investigated in SI engines by a number of researchers [151–153,159,219,220]. Pechout et al. [220] studied the effect of higher level butanol blends 30% and 50%. B30 and B20 indicated lower UHC compared to gasoline. Increasing butanol ratios in the blends leads to increased flame propagation. Another study has been undertaken by Dernotte et al. [221] who evaluated butanol-gasoline blends with ratios of 0–80%. For the 40% Butanol-60% gasoline blend, HC emissions were minimal. NO_x emissions saw no significant change. Butanol addition caused an improvement in the stability of combustion and reduced ignition delay. Alasfour et al. [160] studied the effect of 30% butanol on HC emission in a Hydra single-cylinder SI engine. He found that HC emissions can be reduced when 30% isobutanol-gasoline fuel was tested as a result of retarding ignition timing, increasing cooling water temperature, and increasing engine speed levels. Wigg et al. [219] experimentally investigated the effect of n-butanol fuel in a Ford single-cylinder SI engine; and also the results of butanol-gasoline compared to that of gasoline and ethanol at same operating conditions. The experimental result showed that engine performance produced from gasoline and butanol was being a similar with butanol producing slightly less in engine torque. Butanol combustion showed a lower peak temperature which resulted in decreased exhaust gas temperature and NO_x emission. Butanol has a lower peak pressure than gasoline and ethanol. Based on these results it can be stated that butanol offers an increase in engine performance over ethanol while requiring less fuel to be injected. HC emission levels of butanol were three times more than for gasoline fuel. NO_x emission levels of butanol were 17% lower than for gasoline. Tornatore et al. [150] studied the influence of adding butanol to

Table 7
Summary of some research into additive butanol blend for SI and CI engines.

Author	Alcohol	Reference fuel	Engine tested	Butanol %	Test result	Year
Rakopoulos et al. [146]	Butanol	Diesel	4-stroke & DI, 2000 rpm. & at three different loads	8, 16 & 24 n-butanol,	↓Smoke density ↓NO_x & CO ↑HC	2010
Rakopoulos et al. [147]	Butanol	Diesel	6-cylinder,water-cooled, & turbocharged 1200 & 1500 RPM	8 & 16 n-butanol	↓Smoke density ↓NO_x & CO ↑HC	2010
Tornatore et al. [150]	Butanol	Gasoline	Single-cylinder port fuel injection with an external boosting device & Turbocharged	40 n-butanol	Highest luminosity of B40 ↓Ultrafine carbonaceous particles	2012
Gu et al. [151]	Butanol	Gasoline	Single-cylinder & Port fuel-injection. Different spark timings & EGR rates.	10, 30, 40 & 100 n-butanol	↓HC, ↓CO & ↓NO_x ↓PN	2012
Szwaja & Naber [152]	Butanol	Gasoline	Single-cylinder with variable compression ratio	0, 20 & 60 n-butanol	10° BTDC for pure n-butanol Provides maximum efficiency without combustion knock	2010
Dobre et al. [126]	Butanol	Diesel	DI	20 n-butanol	↓5% in BSFC Maximum pressure ↓ ↓NO_x by 25% CO_2 reduced by 10%	2014
Karabektas & Hosoz [130]	Butanol	Diesel	4-stroke, DI, full-load conditions at speeds between 1200 and 2800 rpm with 200 rpm increament.	5, 10, 15 & 20 iso-butanol	↑BSFC 10% isobutanol →↑BTE CO↓ & NO_x ↓ ↑HC	2009
Al-Hasan & Al-Momany [133]	Butanol	Diesel	Single-cylinder, 4-stroke Lister 1–8, 375 to 625 with an increment of 42 rpm	10, 20, 30 & 40 iso-butanol	↓exhaust gas temperature & ↓BP ↑BSFC ↓BTE	2008
Yana et al. [134]	Butanol	Diesel	Single-cylinder, 4-stroke & DI Injection pressure was controlled at 60 or 90 MPa & EGR	Butanol		2014
Armas et al. [117]	Butanol	Diesel	Turbocharged, DI & equipped with common rail injection system & EGR	16 n-butanol	↑ NO_x & ↑HC ↓ CO	2014

Note:↑, increase & ↓, decrease.

gasoline in a port fuel injection single-cylinder SI engine with changes in the spark timing and fuel injection phasing. Adding butanol to gasoline fuel enhanced SI engine to work in more advanced spark timing with normal combustion behaviour. Gu et al. [151] evaluated gas emissions of SI engine operated with n-butanol-gasoline blends in combination with EGR, different spark timings, EGR rates and blend ratios. HC, CO and NO_x emission levels were lower compared with gasoline fuel. From this research, it can be concluded that pure n-butanol increases HC and CO emission levels while it decreases NO_x emission levels compared to those of gasoline. Adding n-butanol to gasoline fuel can decrease PN emissions increases HC, NO_x emissions. However, CO emissions decrease compared with those of gasoline. Furthermore, Szwaja et al. [152] studied the impact of n-butanol on combustion processes in a single-cylinder SI engine with variable compression ratio and different butanol ratios (0%, 20%, and 60%). n-butanol can be directly substituted with gasoline either as a neat fuel or an additive blend for SI engines because of the similar properties of n-butanol.

3.4. Acetone-butanol-ethanol (ABE) in internal combustion engines

Recently, a biofuel mixture of ABE has shown potential as an alternative fuel blend due to its high butanol content. This mixture, which can be produced from fermentation, can later be purified to obtain pure acetone, butanol, and ethanol. However, a number of researchers [168,217,222–225] support the possibility of using the ABE mixture itself as a fuel additive. The elimination of the purification step can result in a significant reduction in production cost. ABE has a high ratio of butanol so it provides a higher energy content compared to ethanol, some physical properties are similar to commercial transportation fuels, and is cheaper to produce than butanol. This fuel has attracted researchers' attention because it is a green energy resource that possibly improves the engine performance and lowers the emissions compared to commercial transportation fuels.

3.4.1. Combustion characteristics of acetone and ABE mixtures

3.4.1.1. Acetone. Acetone (chemical formula C_3H_6O) is one component of ABE mixtures. Acetone has some advantageous chemical properties which can enhance conventional fuel efficiency. One of these properties is the auto-ignition temperature, which is higher than those of ethanol and butanol. Therefore the acetone vapour is probably ignited before other species in the blend. The experimental results found that the acetone content of the ABE mixture is important because it contributes to advancing the combustion phasing [226]. A number of studies investigated the combustion behaviour of acetone and measured its laminar burning velocity and flame speed under different operating conditions.

Gong et al. [227] investigated the laminar flames of C_3 fuels, which are oxygenated (n-propanol and acetone) or not (propane) in a combustion bomb to compare combustion characteristics. The experimental results showed that acetone provides the lowest flame speeds while propanol provides the highest. These results have occurred because propanol has a large number of H atoms which leads to acceleration of the chain branching rate and enhances the oxidation. However, the high concentration of CH_3 in acetone resulted in the lowest H and OH concentrations, leading to chain termination, thereby causing the lowest flame speed. These results also validate the chemical kinetic models.

Pichon et al. [176] investigated the laminar flame speed and ignition delay time of acetone. A kinetic model has been developed to simulate these and data from the literature for acetone and for ketene, which was found to be an important intermediate in its oxidation. Acetone oxidation in argon was studied behind reflected shock waves in the temperature range of 1340–1930 K, at 1 atm and at $\phi = 0.5$, 1 and 2. The results showed that the addition of up to 15% acetone to a stoichiometric n-heptane mixture has no impact on the ignition delay times. Using a spherical bomb, a maximum flame speed of pure acetone in air was obtained at $\sim 35\ \mathrm{cm\ s^{-1}}$ at maximum $\phi = 1.15$, 298 K and 1 atm.

Burluka et al. [228] experimentally and computationally studied laminar flames of three C_3H_6O isomers (propylene oxide, propionaldehyde and acetone). These are representative of cyclic ether, aldehyde and ketone species which are important as intermediates in oxygenated fuel combustion. The experimental results noted significant differences in burning velocity for the three isomers. The burning velocity of the acetone-air mixture was the slowest with propylene oxide-air the fastest.

3.4.1.2. ABE mixture. Wu et al. [226] investigated the spray and combustion characteristics of ABE-diesel with three volume ratios of ABE (20%, 50% and 60%) blended with diesel. The ABE50 blend achieved a shorter ignition delay (slightly longer than that of D100) and combustion duration compared to those of ABE20 and ABE80 because of its relatively low latent heat and improved spray performance. ABE50 was the blend that displayed combustion characteristics similar to pure diesel. It was found that the ignition delay time for all tested fuels is quite similar and short at high ambient temperature conditions, such as 1000 K and 1200 K. The reaction rate was extremely high for all the tested fuels under high ambient temperatures, which is mainly controlled by the fluid dynamics process, i.e., spray atomisation and fuel droplet evaporation. It is known that the boiling points of the fuels (Table 4) are much lower than the high ambient temperatures, 1000 K and 1200 K. Therefore all the tested fuels exhibit very short and similar ignition delays under these conditions.

Another study done by this group [229] blended different component volumetric ratio (A:B:E of 6:3:1; 3:6:1; and pure butanol) with 80% volume diesel and injected the mixtures into a constant volume chamber. The ABE20 (6:3:1) blend presented characteristics of combustion very similar to those of neat diesel and the ignition delay was much shorter than that of the other ABE–diesel blends due to the high fraction of acetone. It can be concluded that the significant advancement of combustion phasing of ABE20 (6:3:1) is due to the effects of the acetone. Firstly, all the individual components of ABE require higher energy than diesel to evaporate, but acetone's latent heat of vaporisation is much lower than those of ethanol and butanol (Table 4). Moreover, the vapour pressure of acetone is significantly higher than those of ethanol and butanol. It is therefore reasonable to assume that acetone is highly volatile and would reach flammability limits first. In addition, acetone has a lower viscosity, higher vapour pressure and lower boiling point, which consequently decreases the combustion duration of different fuels. The auto-ignition temperature of acetone is higher than those of butanol and ethanol, therefore the acetone vapour is probably initially ignited by the flame of diesel. It can be concluded that the acetone content in the ABE mixture is important because it contributes to advancing the combustion phasing.

Van et al. [230] used experiments and kinetic modelling to study pyrolysis and combustion of ABE mixtures. The mechanism of this study was validated with previous published studies regarding pyrolysis and combustion data for the ABE-mixtures. The research group obtained excellent agreement between measured and simulated results. The experimental result found that the laminar flame speed of ABE is higher than that of acetone and lower than that of ethanol and butanol, which agrees with the observed experimental flame speeds. Laminar flame speeds of premixed methanol, ethanol, and n-butanol at atmospheric pressure were recently determined [205] and [170]. These results show that the laminar flame speeds of methanol are higher compared to those of ethanol and the heavier alcohol, under fuel-rich conditions. The laminar flame speed of ABE is higher than that of acetone and lower than that of ethanol and butanol. Thus the octane rating of the ABE mixture is higher when compared with that of pure n-butanol fuel.

Rao et al. [240] investigated the puffing and micro-explosion behaviour of three blend ratios (10%, 30% and 50%) of ABE and butanol blended with jet A-1 fuel. They reported that puffing plays a crucial role in enhancing the micro-explosion especially in droplets with 50/50 composition. The probability of micro-explosion in droplets with ABE was found to be higher than that of butanol blends although bubble growth rate was almost similar for all butanol and ABE blends they concluded that ABE blends showed more advantages compared to butanol blends in enhancing atomisation and combustion efficiency.

3.4.2. ABE blend tested in CI engines

Previously, some researchers have tested the ABE mixture by a number of experimental investigations in CI engines. The early research investigating ABE combustion behaviour experimentally and numerically has been undertaken by Van et al. [230]. The results showed that the detailed mechanism of the pyrolysis and oxidation of ABE contained ≅ 350 species and more than 10,000 reactions. Research also shows that the ABE laminar flame speed is higher than that of acetone and lower than the laminar flame speed of ethanol and butanol. The impact of ABE on various formulations of ABE (A: B: E 6:3:1, 3:6:1 and butanol) and ABE-diesel blends (D100, ABE20, ABE50 and ABE80) on spray and combustion behaviour in a constant-volume chamber has been extensively studied [223,224,226,229,231,232]. The results indicate that: (1) ABE can decrease the ignition delay and combustion temperature; (2) there are remarkable reduction capabilities for soot and NO_x; and (3) the heat release rate curve of ABE20 (6:3:1) was very similar to that of D100 in terms of the ignition delay and initial premixed combustion, while the heat release rate curve of ABE20 (3:6:1) was closer to that of 10 butanol, respectively. The natural flame luminosity was found to be reduced significantly by an increasing ABE ratio due to the fuel-borne oxygen that accelerates soot oxidation along with longer flame lift-off lengths that: effectively decrease the equivalence ratio in the combustion region.

Lin et al. [168] investigated experimentally a common-rail diesel engine fuelled with ABE-diesel blends. The test revealed that: the thermal efficiency consistently increased; and the NO_x and soot emissions were significantly reduced with up to 20% v/v of ABE addition. Zhang et al. [225] studied a semi-detailed chemical reaction mechanism for combustion simulation of ABE with diesel blends used to model ABE-diesel spray combustion in a constant volume chamber. This mechanism was comprised of ABE and n-heptane as alternate fuel species. The KIVA-3V program can be used to simulate the spray dynamics and combustion characteristics inside the constant volume chamber with the aid of multiple sub-models for the spray and validated mechanism. Different sub-models combined (spray breakup, evaporation, turbulence, combustion and droplet collision models) were used to simulate the dynamic behaviour of the spray. Reasonable agreements—in both shock tube simulation and constant volume chamber simulation—of ignition delay, cylinder pressures, and heat release rates were achieved between experimental and simulated results. This mechanism consisted of 262 species and 1509 reactions. Some of these reactions are shown Fig. 9. In brief, a semi-detailed chemical mechanism has been demonstrated to be computationally acceptable in time scales while maintaining the kinetic behaviour of recently-studied ABE-diesel blends.

Zhao et al. [167] investigated experimentally and numerically the soot mechanism of ABE with various oxygen concentrations. A multistep ABE phenomenological soot model was proposed and implemented in the KIVA-3V Release 2 code. At 11% ambient oxygen, both soot formation and oxidation mechanism were suppressed, thus leading to the reduction of soot particles under highly diluted oxygen conditions.

Ma et al. [233] performed a droplet evaporation test of ABE mixture and diesel in a non-combusting droplet chamber at high ambient temperatures. The addition of the ABE mixture enhanced the evaporation speed of the droplet and thus reduced the lifetime of the droplet. Wu et al. [234] investigated optical the impact of ABE on soot distribution. A two-dimensional soot distribution and soot mass of spray combustion of ABE and diesel was measured by forward illumination light extinction (FILE) technology. The soot distribution area and intensity of ABE, especially ABE with a high acetone fraction, is much lower than that of diesel. Quantitative results of soot mass for ABE show that the soot increases rapidly with rates that are largely increased when elevating temperature. In addition, clean combustion of ABE benefited from a lean air-fuel mixture due to greater volatility and low stoichiometric ratio of the fuel. Soot produced from ABE is much lower than diesel. Furthermore, Chang et al. [217] investigated diesel mixed with different ABE ratios without dehydration and no surfactant addition with different purities (ABE with water). In addition, these blends were generally stable when water was less than 0.6% of the ABE amount. Furthermore, ABE containing water enhanced BTE by 3.26–8.56%. Moreover, the emissions of PM were reduced by 5.82–61.6%, NO_x emissions reduced by 3.69–16.4%, polycyclic aromatic hydrocarbons (PAHs) reduced by 0.699–31.1%, and the toxicity equivalent of PAHs (BaPeq) reduced by 2.58–40.2%, when compared to regular diesel. The same authors [222] studied ABE (5:14:1) mixture with 2% water by volume as an additive to a diesel-biodiesel blend in different additive ratios. All the blends were stable at these ratios. Biodiesel had greater NO_x emissions, the blends that contained 2.5% of the water-containing ABE solution had significantly lower NO_x (4.30–30.7%), PM (10.9–63.1%), and PAHs emissions (26.7–67.6%) than the biodiesel-diesel blends and regular diesel, respectively. Furthermore, BTE of this new blend was 0.372–7.88% higher with respect to both the biodiesel-

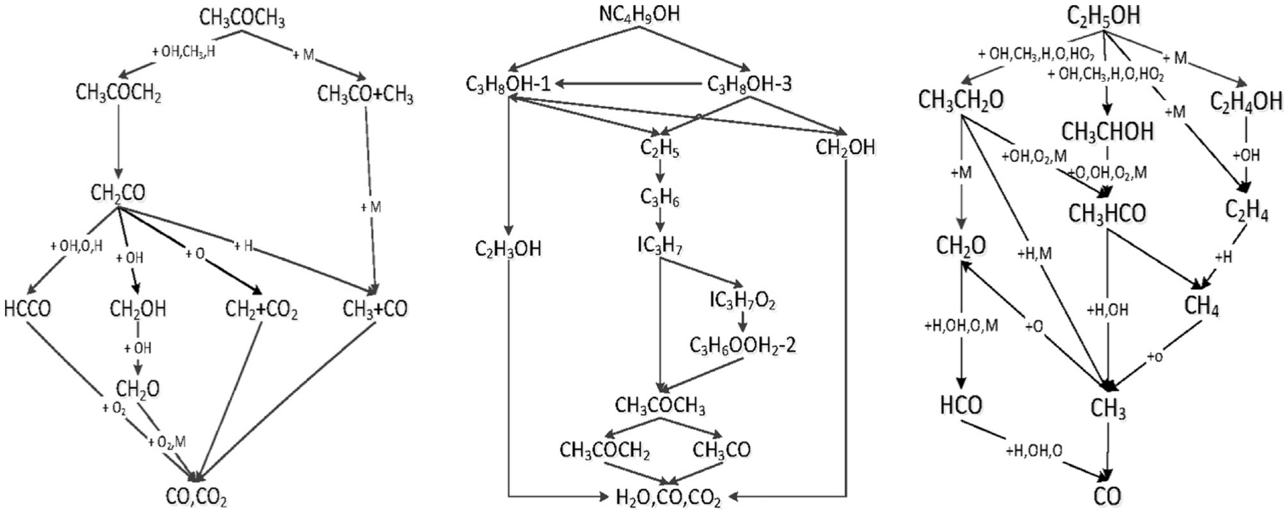


Fig. 9. Primary reaction pathway of acetone, ethanol and butanol [225].

diesel blends and regular diesel. Table 8 presents different results in terms of engine performance and emissions of ethanol as a blend additive for diesel fuel.

3.4.3. ABE blend tested in SI engines

As mentioned above, research related to ABE as an alternative fuel is still in the early phase. Most research deals with the combustion and emissions performance of ABE-diesel blends in diesel engines, while studies related to SI engines fuelled by ABE-gasoline blends is still not sufficient. Nithyanandan et al. [235] performed a preliminary investigation into the performance and emissions of a port-fuel injected SI engine fuelled with ABE and gasoline with volumetric ratios of 0%, 20%, and 40%. Moreover, pure gasoline was also used as a baseline for comparison of ABE fuels. The peak pressure of ABE20 was higher than gasoline; and ABE40 showed a lower peak pressure. ABE20 featured a shorter ignition delay and an advanced 50% MFB (mass fraction burned) location, which could be attributed to ABE's higher laminar flame speed. BSFC increased gradually with increasing ABE fraction, due to the lower energy content of the blends and thus more fuel was required to match the power output of gasoline. CO and UHC emissions increased for ABE20 because of slight enhancements in air/fuel mixing and more fuel being partly oxidized. However, ABE40 showed decreased CO and increased UHC emissions due to a deterioration in combustion quality with some of the fuel not even being partially oxidized. Another study by the same authors [236] considered the effect of ABE and gasoline blends ranging from 0% to 80% vol. in a port fuel injected Ford single-cylinder SI engine. The trace pressure of all the blends was slightly lower than that of gasoline, while trace pressure of ABE80 showed a slightly higher and advanced peak relative to gasoline. ABE additive to gasoline resulted in an increase in BSFC, while the exhaust gas temperature and NO_x emissions showed that ABE combusts at a lower peak temperature. CO emissions were lower and UHC emissions were higher compared to those of gasoline. Furthermore, Li et al. [178] studied the combustion and emissions performance of a SI engine fuelled with ABE with water containing water and gasoline blends (ABE29.5W0.5, ABE30 and ABE0 (pure gasoline)). Engine torque and BTE of ABE29.5W0.5 were being enhanced by 9.6–12.7% and 5.2–11.6% compared to pure gasoline, respectively. ABE29.5W0.5 also presented similar BSFC to pure gasoline. According to the MFB, ABE29.5W0.5 blend showed a longer ignition delay and combustion duration. This means ABE29.5W0.5 blend had a lower combustion rate because of combustion temperature reduction due to water addition. Additionally, ABE29.5W0.5 blend produced lower NO_x and CO emissions while UHC was increased than those of pure gasoline.

Another study done by the same authors [237] also evaluated the effect of water-containing ABE-gasoline blends (ABE30, ABE85, ABE29.5W0.5 and ABE29W1) in an SI engine. Engine torque of ABE29W1 blend was higher by (3.1–8.2%) than those of gasoline. CO, HC and NO_x emissions were also lower by (9.8–35.1%), (27.4–78.2%) and (4.1–39.4%) respectively than those of gasoline. Zhang et al. [238] studied a comparison of high-alcohol-content gasoline blends in SI engines. They compared ethanol, butanol and ABE as fuel blends for internal combustion engines. E85 had the highest peak in-cylinder pressure and most advanced combustion phasing, while B85 had the lowest peak pressure and most retarded phasing. The longest ignition delay of B85 is mainly because butanol has a low vapour pressure leading to relatively poor evaporation. Ignition delay and combustion duration decreased with increasing equivalence ratio. All three alcohol-containing fuels had slightly lower BTE and higher BSFC under the same stoichiometric conditions. Under stoichiometric conditions, B85 shows much higher HC and CO emissions than the other three fuels. Poor evaporation of butanol leads to incomplete combustion. E85, B85, and ABE85 have lower NO_x emissions than gasoline due to the combined effects of adiabatic flame temperature and heat capacity. Nithyanandan et al. [239] studied the performance of different ABE blends (A:B:E of 3:6:1, 6:3:1 and 5:14:1) to determine the best blend as an additive for gasoline fuel. The peak pressure of the ABE blends was slightly higher than that of gasoline, however ABE (3:6:1) mixture also presented an advanced peak relative to gasoline. Increasing n-butanol ratio in the blend showed advanced combustion phasing due higher flame speed (45 m/s) of butanol. BSFC increased gradually with the ABE blends, due to the lower energy content of the blends and thus more fuel was required to match the power output of gasoline. Increasing n-butanol in the blend showed increased HC and CO emissions due to incomplete combustion. In contrast, ABE (6:3:1) blend showed reduced HC emissions, while NO_x emissions showed no recognizable changes between gasoline, ABE (6:3:1) and ABE (3:6:1). These results were supported by the minor variations in exhaust gas temperature (Table 9).

4. Conclusions and future prospects

A decade ago, the commercial production of ABE via fermentation of biomass was not feasible due to the low ABE yield. Nowadays, some improvements are occurring as a result of developments in the genetic engineering and pre-treatment processes. These improvements have led to an increase in ABE yield, making ABE a potential blend for both diesel and gasoline fuels.

Literature reviews showed that n-butanol presents higher laminar burning velocity and shorter ignition delay times than the other three butanol isomers, with sec-butanol and tert-butanol the least reactive. The laminar flame speed of ABE mixtures is higher than that of acetone and lower than that of ethanol and butanol. The kinetic aspect of H and OH radicals play a major role in laminar speeds.

Butanol is a better blend than ethanol in diesel regarding: blend stability, blend properties, engine performance and reduction in some types of emissions. However, the main obstacle for using butanol is the high cost of production due to the high cost of recovery from the ABE mixture.

ABE has a high butanol percentage so it provides higher energy content compared to ethanol and is cheaper to produce compared to butanol. The experimental results of testing a blend of ABE and diesel fuel revealed the following: (1) it can decrease the ignition delay and combustion temperature; (2) soot and NO_x were remarkably reduced; (3) thermal efficiency consistently increased with more ABE (up to 10%); (4) the addition of the ABE mixture has enhanced the evaporation speed of fuel droplets, thus reducing droplet lifetime and resulting in improving combustion efficiency. The use of ABE with low purity (ABE and water) as a fuel additive for diesel fuel without dehydration and surfactant addition is another technique that can be applied to decrease the recovery cost and improve the engine performance.

With regard to the experimental results of operating ABE as a blend for gasoline fuel in SI engines, the emission data indicated that: (1) CO decreased when adding ABE20; (2) no major changes in NO_x were obtained between gasoline and ABE (3:6:1), which was supported by exhaust gas temperature that exhibited a minor change; (3) BSFC increased gradually with the ABE additive, this is because more fuel was

Table 8

Pre-exponential factors of modified reactions adapted from [225].

Reaction	Original pre-exponential factor	New pre-exponential factor
CH3COCH3(+M) < = > CH3CO+CH3(+M)	7.11×10^{21}	1.76×10^{22}
CH3COCH3+H < = > CH3COCH2+H2	9.8×10^{5}	6.14×10^{5}
C2H5OH+M=CH3+CH2OH+M	5.94×10^{23}	3.22×10^{23}
C2H5OH+M=C2H4+H2O+M	2.79×10^{13}	8.18×10^{13}
C2H5OH+HO2 =C2H4OH+H2O2	8.20×10^{3}	2.53×10^{4}
NC4H9OH+HO2 < = > C4H8OH-1+H2O2	6.00×10^{12}	0.93×10^{15}
C7H15-2 < = > C7H14-2+H	6.067×10^{12}	7.72×10^{11}

Table 9
Summary of some research into additive ABE as additive blend for CI and SI engine.

Author	Alcohol	Reference fuel	Engine tested	ABE%	Test results	Year
Chang et al. [222]	ABE	Diesel	Single-cylinder, 4-stroke, air-cooled & DI	5, 10 & 15 ABE	↑ BSFC; 20 ABE ↑particle number	2014
Nithyanandan et al. [236]	ABE	Gasoline	PFI engine speed of 1200 RPM under different equivalence ratios	0–80 ABE	ABE80 slightly ↑BP ↑HC ↓NO$_x$	2014
Zhang et al. [238]	ABE	Gasoline	Single-cylinder, V8 200 Ford 1200 RPM, $\Phi = 0.83-1.25$, BMEP = 3 bar.	ABE 85	ABE 85 slightly ↓BTE & fairly↑ higher BSFC. ↑HC & ↓ CO ABE85 ↓NO$_x$ than gasoline	2015
Nithyanandan et al. [239]	ABE	Gasoline	PFI Engine speed of 1200 RPM and loads of 3 and 5 bar (BMEP) under different equivalence ratio	A:B:E ratios of 3:6:1, 6:3:1 & 5:14:1	↓BSFC ↑BTE ABE (6:3:1) ↑HC & ↓CO No major change.	2016

Note:↑, increase & ↓, decrease.

required to match the power output of gasoline due to the lower energy content of the blends; (4) ABE29.5W0.5 blend also produced a similar BSFC to pure gasoline and a longer ignition delay, which meant that ABE29.5W0.5 had a lower combustion rate because of the combustion temperature reduction due to water addition. Moreover, NO$_x$ and CO emissions were lower while UHC emissions were higher than those of pure gasoline.

In brief, this literature review concludes the following: using ABE as an additive blend for diesel and gasoline presented a number of advantages in related to improve engine performance such as thermal efficiency and reduce engine emissions such as NO$_x$, CO, soot emission and combustion temperature; there is a lack of studies related to operating ABE-diesel and ABE-biodiesel-diesel mixtures in CI engines; and ABE-gasoline in SI engines. In addition, there are limited studies related to the butanol-acetone (BA) blend in both CI and SI engines. Furthermore, there are very few studies regarding low purity ABE and BA blends tested in CI or SI engines, respectively. Therefore, the authors see the need for more research in this field.

Acknowledgments

The first author thanks the Iraqi Government Ministry of Higher Education and Scientific Research for supporting the research.

References

[1] Savaliya ML, Dhorajiya BD, Dholakiya BZ. Recent advancement in production of liquid biofuels from renewable resources: a review. Res Chem Intermed 2013;41(2):475–509.

[2] Ashraful A, Masjuki H, Kalam M, Fattah IR, Imtenan S, Shahir S, Mobarak H. Production and comparison of fuel properties, engine performance, and emission characteristics of biodiesel from various non-edible vegetable oils: a review. Energy Convers Manag 2014;80:202–28.

[3] Ranjan A, Moholkar VS. Comparative study of various pretreatment techniques for rice straw saccharification for the production of alcoholic biofuels. Fuel 2013;112:567–71.

[4] Zhang WL, Liu ZY, Liu Z, Li FL. Butanol production from corncob residue using Clostridium beijerinckii NCIMB 8052. Lett Appl Microbiol 2012;55(3):240–6.

[5] Laza T, Laza Á. Basic fuel properties of rapeseed oil-higher alcohols blends. Fuel 2011;90(2):803–10.

[6] Zhang Y, Hou T, Li B, Liu C, Mu X, Wang H. Acetone-butanol-ethanol production from corn stover pretreated by alkaline twin-screw extrusion pretreatment. Bioprocess Biosyst Technol 2014;37(5):913–21.

[7] No S-Y. Inedible vegetable oils and their derivatives for alternative diesel fuels in CI engines: a review. Renew Sustain Energy Rev 2011;15(1):131–49.

[8] Imtenan S, Varman M, Masjuki HH, Kalam MA, Sajjad H, Arbab MI, Rizwanul Fattah IM. Impact of low temperature combustion attaining strategies on diesel engine emissions for diesel and biodiesels: a review. Energy Convers Manag 2014;80:329–56.

[9] Singh-Nee Nigam P, Banat I, Singh D, McHale A, Marchant R. Continuous ethanol production by thermotolerant Kluyveromyces marxianus IMB3 immobilized on mineral kissiris at 45 °C. World J Microbiol Biotechnol 1997;13(3):283–8.

[10] Love G, Gough S, Brady D, Barron N, Nigam P, Singh D, Marchant R, McHale A. Continuous ethanol fermentation at 45 °C using Kluyveromyces marxianus IMB3 immobilized in calcium alginate and kissiris. Bioprocess Eng 1998;18(3):187–9.

[11] Zhao R, Bean S, Wang D, Park S, Schober T, Wilson J. Small-scale mashing procedure for predicting ethanol yield of sorghum grain. J Cereal Sci 2009;49(2):230–8.

[12] Gibbons WR, Westby CA. Cofermentation of sweet sorghum juice and grain for production of fuel ethanol and distillers' wet grain. Biomass 1989;18(1):43–57.

[13] Limayem A, Ricke SC. Lignocellulosic biomass for bioethanol production: current perspectives, potential issues and future prospects. Prog Energy Combust Sci 2012;38(4):449–67.

[14] Alvira P, Tomás-Pejó E, Ballesteros M, Negro MJ. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review. Bioresour Technol 2010;101(13):4851–61.

[15] Galbe M, Zacchi G. Pretreatment of lignocellulosic materials for efficient bioethanol production, in biofuels. Springer; 2007. p. 41–65.

[16] Sarkar N, Ghosh SK, Bannerjee S, Aikat K. Bioethanol production from agricultural wastes: an overview. Renew Energy 2012;37(1):19–27.

[17] Ezeji TC, Qureshi N, Blaschek HP. Bioproduction of butanol from biomass: from genes to bioreactors. Curr Opin Biotechnol 2007;18(3):220–7.

[18] Ramey D. Butanol advances in biofuels. The Light Party.; 2004.

[19] Qureshi N, Saha BC, Dien B, Hector RE, Cotta MA. Production of butanol (a biofuel) from agricultural residues: Part I – use of barley straw hydrolysate. Biomass Bioenergy 2010;34(4):559–65.

[20] Qureshi N, Ezeji TC. Butanol,'a superior biofuel'production from agricultural residues (renewable biomass): recent progress in technology. Biofuels Bioprod Bioref 2008;2(4):319–30.

[21] Nigam PS, Singh A. Production of liquid biofuels from renewable resources. Prog Energy Combust Sci 2011;37(1):52–68.

[22] Hamawand I, Sandell G, Pittaway P, Chakrabarty S, Yusaf T, Chen G, Seneweera S, Al-Lwayzy S, Bennett J, Hopf J. Bioenergy from Cotton Industry Wastes: a review and potential. Renew Sustain Energy Rev 2016;66:435–48.

[23] Ghadikolaei MA. Effect of alcohol blend and fumigation on regulated and unregulated emissions of IC engines—a review. Renew Sustain Energy Rev 2016;57:1440–95.

[24] Li X, Li Z-G, Shi Z-P. Metabolic flux and transcriptional analysis elucidate higher butanol/acetone ratio feature in ABE extractive fermentation by Clostridium acetobutylicum using cassava substrate. Bioresour Bioprocess 2014;1(1):1–13.

[25] García V, Päkkilä J, Ojamo H, Muurinen E, Keiski RL. Challenges in biobutanol production: how to improve the efficiency? Renew Sustain Energy Rev 2011;15(2):964–80.

[26] Weizmann C. Improvements in the bacterial fermentation of carbohydrates and in bacterial cultures for the same. Symbiotic Assoc Biotechnol Appl Microbiol 1915;1.

[27] Jones DT, Woods DR. Acetone-butanol fermentation revisited. Microbiol Rev 1986;50(4):484.

[28] Killeffer DH. Butanol and acetone from Corn1: a description of the fermentation process. Ind Eng Chem 1927;19(1):46–50.

[29] Crawford G. Development of the butyl-acetonic fermentation industry. Ind Eng Chem 1930;22(11):1163.

[30] Zverlov Berezina, Velikodvorskaya, Schwarz. Bacterial acetone and butanol production by industrial fermentation in the Soviet Union: use of hydrolyzed agricultural waste for biorefinery. Appl Microbiol Biotechnol 2006;71(5):587–97.

[31] Chiao JS, Sun ZH. History of the acetone-butanol-ethanol fermentation industry in China: development of continuous production technology. J Mol Microbiol Biotechnol 2007;13(1–3):12–4.

[32] Ni Y, Sun Z. Recent progress on industrial fermentative production of acetone-butanol-ethanol by Clostridium acetobutylicum in China. Appl Microbiol Biotechnol 2009;83(3):415–23.

[33] Joins Novozymes C. DuPont and BP disclose advanced biofuels partnership targeting multiple butanol isomers. Chem Eng News 2008;86(3).

[34] Jones DT, Shirley M, Wu X, Keis S. Bacteriophage infections in the industrial acetone butanol(AB) fermentation process. J Mol Microbiol Biotechnol 2000;2(1):21–6.

[35] Nimcevic D, Gapes JR. The acetone-butanol fermentation in pilot plant and pre-industrial scale. J Mol Microbiol Biotechnol 2000;2(1):15–20.

[36] Kittithanesuan N, Phisalaphong M. Enhanced acetone-butanol production from

sugarcane juice by immobilized Clostridium acetobutylicum (ATCC 824) on thin-shell silk cocoons. Biotechnol Bioprocess Eng 2015;20(3):599–607.
[37] He Q, Chen H. Improved efficiency of butanol production by absorbed lignocellulose fermentation. J Biosci Bioeng 2013;115(3):298–302.
[38] Qureshi N, Ezeji TC, Ebener J, Dien BS, Cotta MA, Blaschek HP. Butanol production by Clostridium beijerinckii. Part I: use of acid and enzyme hydrolyzed corn fiber. Bioresour Technol 2008;99(13):5915–22.
[39] Chen H, Han Y, Xu J. Simultaneous saccharification and fermentation of steam exploded wheat straw pretreated with alkaline peroxide. Process Biochem 2008;43(12):1462–6.
[40] Kandasamy M, Hamawand I, Bowtell L, Seneweera S, Chakrabarty S, Yusaf T, Shakoor Z, Algayyim S, Eberhard F. Investigation of ethanol production potential from lignocellulosic material without enzymatic hydrolysis using the ultrasound technique. Energies 2017;10(1):62.
[41] Gnansounou E, Dauriat A, Wyman C. Refining sweet sorghum to ethanol and sugar: economic trade-offs in the context of North China. Bioresour Technol 2005;96(9):985–1002.
[42] Cai D, Zhang T, Zheng J, Chang Z, Wang Z, Qin P-Y, Tan T-W. Biobutanol from sweet sorghum bagasse hydrolysate by a hybrid pervaporation process. Bioresour Technol 2013;145:97–102.
[43] Isar J, Joshi H, Rangaswamy V. n-butanol production from acid-pretreated Jatropha seed cake by Clostridium acetobutylicum. BioEnergy Res 2013;6(3):991–9.
[44] Li HG, Luo W, Wang Q, Yu XB. Direct fermentation of gelatinized cassava starch to acetone, butanol, and ethanol using Clostridium acetobutylicum mutant obtained by atmospheric and room temperature plasma. Appl Biochem Biotechnol 2014;172(7):3330–41.
[45] Moradi F, Amiri H, Soleimanian-Zad S, Ehsani MR, Karimi K. Improvement of acetone, butanol and ethanol production from rice straw by acid and alkaline pretreatments. Fuel 2013;112:8–13.
[46] Yang M, Zhang J, Kuittinen S, Vepsalainen J, Soininen P, Keinanen M, Pappinen A. Enhanced sugar production from pretreated barley straw by additive xylanase and surfactants in enzymatic hydrolysis for acetone-butanol-ethanol fermentation. Bioresour Technol 2015;189:131–7.
[47] Huesemann MH, Kuo L-J, Urquhart L, Gill GA, Roesijadi G. Acetone-butanol fermentation of marine macroalgae. Bioresour Technol 2012;108:305–9.
[48] Qureshi N, Blaschek H. ABE production from corn: a recent economic evaluation. J Ind Microbiol Biotechnol 2001;27(5):292–7.
[49] Kheyrandish M, Asadollahi MA, Jeihanipour A, Jeihanipour, Mohsen, Rismani-Yazdi H, Karimi K. Direct production of acetone–butanol–ethanol from waste starch by free and immobilized Clostridium acetobutylicum. Fuel 2015;142:129–33.
[50] Ezeji T, Blaschek HP. Fermentation of dried distillers' grains and solubles (DDGS) hydrolysates to solvents and value-added products by solventogenic clostridia. Bioresour Technol 2008;99(12):5232–42.
[51] Yang M, Kuittinen S, Zhang J, Vepsäläinen J, Keinänen M, Pappinen A. Co-fermentation of hemicellulose and starch from barley straw and grain for efficient pentoses utilization in acetone–butanol–ethanol production. Bioresour Technol 2015;179:128–35.
[52] Thang VH, Kobayashi G. A novel process for direct production of acetone–butanol–ethanol from native starches using granular starch hydrolyzing enzyme by Clostridium saccharoperbutylacetonicum N1-4. Appl Biochem Biotechnol 2014;172(4):1818–31.
[53] Qureshi N, Saha BC, Hector RE, Dien B, Hughes S, Liu S, Iten L, Bowman MJ, Sarath G, Cotta MA. Production of butanol (a biofuel) from agricultural residues: Part II – use of corn stover and switchgrass hydrolysates. Biomass Bioenergy 2010;34(4):566–71.
[54] Abd-Alla MH, Zohri AN, El-Enany AW, Ali SM. Acetone-butanol-ethanol production from substandard and surplus dates by Egyptian native Clostridium strains. Anaerobe 2015;32:77–86.
[55] Abd-Alla MH, Elsadek El-Enany A-W. Production of acetone-butanol-ethanol from spoilage date palm (Phoenix dactylifera L.) fruits by mixed culture of Clostridium acetobutylicum and Bacillus subtilis. Biomass Bioenergy 2012;42:172–8.
[56] Bellido C, Infante C, Coca M, González-Benito G, Lucas S, García-Cubero MT. Efficient acetone–butanol–ethanol production by Clostridium beijerinckii from sugar beet pulp. Bioresour Technol 2015;190:332–8.
[57] Naik SN, Goud VV, Rout PK, Dalai AK. Production of first and second generation biofuels: a comprehensive review. Renew Sustain Energy Rev 2010;14(2):578–97.
[58] Jin C, Yao M, Liu H, Lee C-fF, Ji J. Progress in the production and application of n-butanol as a biofuel. Renew Sustain Energy Rev 2011;15(8):4080–106.
[59] Mata TM, Martins AA, Caetano NS. Microalgae for biodiesel production and other applications: a review. Renew Sustain Energy Rev 2010;14(1):217–32.
[60] Ben-Ghedalia D, Miron J. The effect of combined chemical and enzyme treatments on the saccharification and in vitro digestion rate of wheat straw. Biotechnol Bioeng 1981;23(4):823–31.
[61] Haghighi Mood S, Hossein Golfeshan A, Tabatabaei M, Salehi Jouzani G, Najafi GH, Gholami M, Ardjmand M. Lignocellulosic biomass to bioethanol, a comprehensive review with a focus on pretreatment. Renew Sustain Energy Rev 2013;27:77–93.
[62] Chiaramonti D, Prussi M, Ferrero S, Oriani L, Ottonello P, Torre P, Cherchi F. Review of pretreatment processes for lignocellulosic ethanol production, and development of an innovative method. Biomass Bioenergy 2012;46:25–35.
[63] Prasad S, Singh A, Joshi H. Ethanol as an alternative fuel from agricultural, industrial and urban residues. Resour Conserv Recycl 2007;50(1):1–39.
[64] Vidal PF, Molinier J. Ozonolysis of lignin—improvement of in vitro digestibility of poplar sawdust. Biomass 1988;16(1):1–17.
[65] Von Sivers M, Zacchi G. A techno-economical comparison of three processes for the production of ethanol from pine. Bioresour Technol 1995;51(1):43–52.
[66] Tarkow H, FEIST WC. A mechanism for improving the digestibility of lignocellulosic materials with dilute alkali and liquid ammonia. ACS Publications; 1969.
[67] Morjanoff P, Gray P. Optimization of steam explosion as a method for increasing susceptibility of sugarcane bagasse to enzymatic saccharification. Biotechnol Bioeng 1987;29(6):733–41.
[68] Singh A, Kumar P, Schügerl K. Bioconversion of cellulosic materials to ethanol by filamentous fungi, in enzymes and products from bacteria fungi and plant cells. Springer; 1992. p. 29–55.
[69] Dien BS, Nichols NN, O'bryan PJ, Bothast RJ. Development of new ethanologenic Escherichia coli strains for fermentation of lignocellulosic biomass. Appl Biochem Biotechnol 2000;84(1–9):181–96.
[70] Qureshi N, Saha BC, Hector RE, Cotta MA. Removal of fermentation inhibitors from alkaline peroxide pretreated and enzymatically hydrolyzed wheat straw: production of butanol from hydrolysate using Clostridium beijerinckii in batch reactors. Biomass Bioenergy 2008;32(12):1353–8.
[71] Nasib BC, Sahaa RE, Hectora SR, Hughes, Cottaa MA. Butanol production from wheat straw by simultaneous saccharification and fermentation using Clostridium beijerinckii: Part I—batch fermentation. Biomass Bioenergy 2008;32:168–75.
[72] Celińska E, Grajek W. Biotechnological production of 2,3-butanediol—current state and prospects. Biotechnol Adv 2009;27(6):715–25.
[73] Yang M, Zhang J, Kuittinen S, Vepsäläinen J, Soininen P, Keinänen M, Pappinen A. Enhanced sugar production from pretreated barley straw by additive xylanase and surfactants in enzymatic hydrolysis for acetone–butanol–ethanol fermentation. Bioresour Technol 2015;189:131–7.
[74] Amiri H, Karimi K. Improvement of acetone, butanol, and ethanol production from woody biomass using organosolv pretreatment. Bioprocess Biosyst Eng 2015:1–14.
[75] Ranjan A, Khanna S, Moholkar VS. Feasibility of rice straw as alternate substrate for biobutanol production. Appl Energy 2013;103:32–8.
[76] Gottumukkala LD, Parameswaran B, Valappil SK, Mathiyazhakan K, Pandey A, Sukumaran RK. Biobutanol production from rice straw by a non acetone producing Clostridium sporogenes BE01. Bioresour Technol 2013;145:182–7.
[77] Huang Wei-cho RDE, Shang-Tian Yang. Continuous production of butanol by Clostridium acetobutylicum immobilized in a fibrous bed bioreactor. Appl Biochem Biotechnol 2004;113–116:887–98.
[78] Ellis JT, Hengge NN, Sims RC, Miller CD. Acetone, butanol, and ethanol production from wastewater algae. Bioresour Technol 2012;111:491–5.
[79] Campos-Fernández J, Arnal JM, Gómez J, Dorado MP. A comparison of performance of higher alcohols/diesel fuel blends in a diesel engine. Appl Energy 2012;95:267–75.
[80] Jamuwa D, Sharma D, Soni S. Performance, emission and combustion analysis of an ethanol fuelled stationary CI engine. Biofuels 2016:1–14.
[81] Christensen E, Yanowitz J, Ratcliff M, McCormick RL. Renewable oxygenate blending effects on gasoline properties. Energy Fuels 2011;25(10):4723–33.
[82] Hsieh W-D, Chen R-H, Wu T-L, Lin T-H. Engine performance and pollutant emission of an SI engine using ethanol–gasoline blended fuels. Atmos Environ 2002;36(3):403–10.
[83] Niven RK. Ethanol in gasoline: environmental impacts and sustainability review article. Renew Sustain Energy Rev 2005;9(6):535–55.
[84] Bielaczyc P, Szczotka A, Woodburn J. The Impact of Fuel Ethanol Content on Particulate Emissions from Light-Duty Vehicles Featuring Spark Ignition Engines. SAE Int J Fuels Lubr 2014;7(1):224–35.
[85] Tuner M. Review and benchmarking of alternative fuels in conventional and advanced engine concepts with emphasis on efficiency, CO_2, and regulated emissions. SAE International; 2016.
[86] Ghazikhani M, Hatami M, Safari B, Ganji DD. Experimental investigation of performance improving and emissions reducing in a two stroke SI engine by using ethanol additives. Propuls Power Res 2013;2(4):276–83.
[87] Hansen A, Gratton M, Yuan W. Diesel engine performance and NOX emissions from oxygenated biofuels and blends with diesel fuel. Trans ASABE 2006;49(3):589–95.
[88] Hansen AC, Zhang Q, Lyne PWL. Ethanol–diesel fuel blends—a review. Bioresour Technol 2005;96(3):277–85.
[89] Kumar S, Cho JH, Park J, Moon I. Advances in diesel–alcohol blends and their effects on the performance and emissions of diesel engines. Renew Sustain Energy Rev 2013;22:46–72.
[90] Satgé de Caro P, Mouloungui Z, Vaitilingom G, Berge JC. Interest of combining an additive with diesel–ethanol blends for use in diesel engines. Fuel 2001;80(4):565–74.
[91] Zannis TC, Pariotis EG, Hountalas DT, Rakopoulos DC, Levendis YA. Theoretical study of DI diesel engine performance and pollutant emissions using comparable air-side and fuel-side oxygen addition. Energy Convers Manag 2007;48(11):2962–70.
[92] Tse H, Leung CW, Cheung CS. Investigation on the combustion characteristics and particulate emissions from a diesel engine fueled with diesel-biodiesel-ethanol blends. Energy 2015;83:343–50.
[93] Randazzo ML, Sodré JR. Cold start and fuel consumption of a vehicle fuelled with blends of diesel oil–soybean biodiesel–ethanol. Fuel 2011;90(11):3291–4.
[94] Labeckas G, Slavinskas S, Mažeika M. The effect of ethanol–diesel–biodiesel blends on combustion, performance and emissions of a direct injection diesel engine. Energy Convers Manag 2014;79:698–720.
[95] Huang J, Wang Y, Li S, Roskilly AP, Yu H, Li H. Experimental investigation on the performance and emissions of a diesel engine fuelled with ethanol–diesel blends. Appl Therm Eng 2009;29(11–12):2484–90.

[96] Sayin C. Engine performance and exhaust gas emissions of methanol and ethanol–diesel blends. Fuel 2010;89(11):3410–5.
[97] Kannan D, Pachamuthu S, Nurun Nabi M, Hustad JE, Løvås T. Theoretical and experimental investigation of diesel engine performance, combustion and emissions analysis fuelled with the blends of ethanol, diesel and jatropha methyl ester. Energy Convers Manag 2012;53(1):322–31.
[98] Hansen AC, Lyne PW, Zhang Q. Ethanol-diesel blends: a step towards a bio-based fuel for diesel engines. ASAE Pap 2001:01–6048.
[99] Ajav E, Singh B, Bhattacharya T. Experimental study of some performance parameters of a constant speed stationary diesel engine using ethanol–diesel blends as fuel. Biomass Bioenergy 1999:357–65.
[100] Shi X, Yu Y, He H, Shuai S, Wang J, Li R. Emission characteristics using methyl soyate–ethanol–diesel fuel blends on a diesel engine. Fuel 2005;84(12–13):1543–9.
[101] Li D-G, Zhen H, Xingcai L, Wu-gao Z, Jian-Guang Y. Physico-chemical properties of ethanol–diesel blend fuel and its effect on performance and emissions of diesel engines. Renew Energy 2005;30(6):967–76.
[102] Subbaiah GV, Gopal KR, Hussain SA, Prasad BD, Reddy KT. Rice bran oil biodiesel as an additive in diesel-ethanol blends for diesel engines. Int J Res Rev Appl Sci 2010;3(3):334–42.
[103] Shahir SA, Masjuki HH, Kalam MA, Imran A, Ashraful AM. Performance and emission assessment of diesel–biodiesel–ethanol/bioethanol blend as a fuel in diesel engines: a review. Renew Sustain Energy Rev 2015;48:62–78.
[104] Tse H, Leung CW, Cheung CS, Investigation on the combustion characteristics and particulate emissions from a diesel engine fueled with diesel-biodiesel-ethanol blends. Energy. p. 1–8.
[105] İleri E. Experimental investigation of the effect of diesel–cotton oil–n-butanol ternary blends on phase stability, engine performance and exhaust emission parameters in a diesel engine. Fuel 2013;109:503–11.
[106] Shahir SA, Masjuki HH, Kalam MA, Imran A, Fattah IMR, Sanjid A. Feasibility of diesel–biodiesel–ethanol/bioethanol blend as existing CI engine fuel: an assessment of properties, material compatibility, safety and combustion. Renew Sustain Energy Rev 2014;32:379–95.
[107] Barabás I, Todoruţ I-A. Utilization of biodiesel-diesel-ethanol blends in CI engine. Biodiesel-quality, emissions and by-products. InTech; 2011. p. 215–34.
[108] Chen H, Wang J, Shuai S, Chen W. Study of oxygenated biomass fuel blends on a diesel engine. Fuel 2008;87(15–16):3462–8.
[109] Park SH, Cha J, Lee CS. Impact of biodiesel in bioethanol blended diesel on the engine performance and emissions characteristics in compression ignition engine. Appl Energy 2012;99:334–43.
[110] Suwannakij K, Baitiang T, Tongroon M, Supasitmongkol S. The effects of ethanol-diesel-biodiesel blends on fuel properties. Key Eng Mater 2013;545:89–94.
[111] Yilmaz N. Comparative analysis of biodiesel–ethanol–diesel and biodiesel–methanol–diesel blends in a diesel engine. Energy 2012;40(1):210–3.
[112] Pidol L, Lecointe B, Starck L, Jeuland N. Ethanol–biodiesel–diesel fuel blends: performances and emissions in conventional diesel and advanced low temperature combustions. Fuel 2012;93:329–38.
[113] Hulwan DB, Joshi SV. Performance, emission and combustion characteristic of a multicylinder DI diesel engine running on diesel–ethanol–biodiesel blends of high ethanol content. Appl Energy 2011;88(12):5042–55.
[114] Cheenkachorn K, Fungtammasan B. An investigation of diesel-ethanol-biodiesel blends for diesel engine: Part 2—emission and engine performance of a light-duty truck. Energy Sources Part A: Recovery Util Environ Eff 2010;32(10):894–900.
[115] Guarieiro LLN, de Souza AF, Torres EA, de Andrade JB. Emission profile of 18 carbonyl compounds, CO, CO_2, and NOx emitted by a diesel engine fuelled with diesel and ternary blends containing diesel, ethanol and biodiesel or vegetable oils. Atmos Environ 2009;43(17):2754–61.
[116] Ribeiro NM, Pinto AC, Quintella CM, Da Rocha GO, Teixeira LS, Guarieiro LL, do Carmo M, Rangel, Veloso MC, Rezende MJ, Serpa da Cruz R. The role of additives for diesel and diesel blended (ethanol or biodiesel) fuels: a review. Energy Fuels 2007;21(4):2433–45.
[117] Armas O, García-Contreras R, Ramos Á. Pollutant emissions from new European driving cycle with ethanol and butanol diesel blends. Fuel Process Technol 2014;122:64–71.
[118] Chotwichien A, Luengnaruemitchai A, Jai-In S. Utilization of palm oil alkyl esters as an additive in ethanol–diesel and butanol–diesel blends. Fuel 2009;88(9):1618–24.
[119] Lapuerta M, Armas O, Herreros JM. Emissions from a diesel–bioethanol blend in an automotive diesel engine. Fuel 2008;87(1):25–31.
[120] Tsang KS, Zhang ZH, Cheung CS, Chan TL. Reducing emissions of a diesel engine using fumigation ethanol and a diesel oxidation catalyst. Energy Fuels 2010;24(11):6156–65.
[121] Broukhiyan E, Lestz S. Ethanol fumigation of a light duty automotive diesel engine, SAE Technical Paper; 1981.
[122] Hayes TK, Savage L, White R, Sorenson S. The effect of fumigation of different ethanol proofs on a turbocharged diesel engine. Warrendale, PA: Society of Automotive Engineers; 1988.
[123] Giakoumis EG, Rakopoulos CD, Dimaratos AM, Rakopoulos DC. Exhaust emissions with ethanol or n-butanol diesel fuel blends during transient operation: a review. Renew Sustain Energy Rev 2013;17:170–90.
[124] Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Prog Energy Combust Sci 2007;33(3):233–71.
[125] Juan JC, Kartika DA, Wu TY, Hin T-YY. Biodiesel production from jatropha oil by catalytic and non-catalytic approaches: an overview. Bioresour Technol 2011;102(2):452–60.
[126] Dobre A, Pana C, Nuţu N, Negurescu N, Cernat A, Bondoc I. Bio-butanol-alternative fuel for Diesel engine. INMATEH-Agric Eng 2014;42:145–52.
[127] Lujaji F, Kristóf L, Bereczky A, Mbarawa M. Experimental investigation of fuel properties, engine performance, combustion and emissions of blends containing croton oil, butanol, and diesel on a CI engine. Fuel 2011;90(2):505–10.
[128] Zhang Z-H, Balasubramanian R. Influence of butanol–diesel blends on particulate emissions of a non-road diesel engine. Fuel 2014;118:130–6.
[129] Liu H, Lee C, Huo M, Yao M. Comparison of ethanol and butanol as additives in soybean biodiesel using a constant volume combustion chamber. Energy Fuels 2011;25(4):1837–46.
[130] Karabektas M, Hosoz M. Performance and emission characteristics of a diesel engine using isobutanol–diesel fuel blends. Renew Energy 2009;34(6):1554–9.
[131] Altum S, Öner C, Yaşar F, Adin H. Effect of n-butanol blending with a blend of diesel and biodiesel on performance and exhaust emissions of a diesel engine. Ind Eng Chem Res 2011;50(15):9425–30.
[132] Atmanli A, Ileri E, Yuksel B, Yilmaz N. Extensive analyses of diesel–vegetable oil–n-butanol ternary blends in a diesel engine. Appl Energy 2015;145:155–62.
[133] Al-Hasan MI, Al-Momany M. The effect of iso-butanol-diesel blends on engine performance. Transport 2008;23(4):306–10.
[134] Yanai T, Han X, Wang M, Reader GT, Zheng M, Tjong J. Clean combustion in a diesel engine using direct injection of neat n-butanol. SAE Int J Engines 2014;1.
[135] Jeftić M, Tjong J, Reader G, Wang M, Zheng M. Combustion and exhaust gas speciation analysis of diesel and butanol post injection. SAE Int J Engines 2015;1.
[136] Deep A, Kumar N, Kumar M, Singh A, Gupta D, Patel JS. Performance and emission studies of diesel engine fuelled with orange peel oil and N-butanol alcohol blends, SAE International; 2015.
[137] Mittal N, Patanwal P, Sithananthan M, Subramanian M, Sehgal AK, Suresh R, Das BP. Experimental investigation of n-butanol diesel fuel blends on a passenger car. SAE Int J Engines 2015;1.
[138] Zoldy M, Hollo A, Thernesz A. Butanol as a diesel extender option for internal combustion engines. SAE Int J Engines 2010.
[139] Atmanlı A, Yüksel B, İleri E, Karaoglan A Deniz. Response surface methodology based optimization of diesel–n-butanol –cotton oil ternary blend ratios to improve engine performance and exhaust emission characteristics. Energy Convers Manag 2015;90:383–94.
[140] Rakopoulos DC. Combustion and emissions of cottonseed oil and its bio-diesel in blends with either n-butanol or diethyl ether in HSDI diesel engine. Fuel 2013;105:603–13.
[141] Siwale L, Kristóf L, Adam T, Bereczky A, Mbarawa M, Penninger A, Kolesnikov A. Combustion and emission characteristics of n-butanol/diesel fuel blend in a turbo-charged compression ignition engine. Fuel 2013;107:409–18.
[142] Rakopoulos DC, Rakopoulos CD, Papagiannakis RG, Kyritsis DC. Combustion heat release analysis of ethanol or n-butanol diesel fuel blends in heavy-duty DI diesel engine. Fuel 2011;90(5):1855–67.
[143] Doğan O. The influence of n-butanol/diesel fuel blends utilization on a small diesel engine performance and emissions. Fuel 2011;90(7):2467–72.
[144] Mehta RN, Chakraborty M, Mahanta P, Parikh PA. Evaluation of fuel properties of butanol− biodiesel− diesel blends and their impact on engine performance and emissions. Ind Eng Chem Res 2010;49(16):7660–5.
[145] Lebedevas S, Lebedeva G, Sendzikiene E, Makareviciene V. Investigation of the performance and emission characteristics of biodiesel fuel containing butanol under the conditions of diesel engine operation. Energy Fuels 2010;24(8):4503–9.
[146] Rakopoulos D, Rakopoulos C, Giakoumis E, Dimaratos A, Kyritsis D. Effects of butanol–diesel fuel blends on the performance and emissions of a high-speed DI diesel engine. Energy Convers Manag 2010;51(10):1989–97.
[147] Rakopoulos D, Rakopoulos C, Hountalas D, Kakaras E, Giakoumis E, Papagiannakis R. Investigation of the performance and emissions of bus engine operating on butanol/diesel fuel blends. Fuel 2010;89(10):2781–90.
[148] Balamurugan T, Nalini R. Experimental investigation on performance, combustion and emission characteristics of four stroke diesel engine using diesel blended with alcohol as fuel. Energy 2014;78:356–63.
[149] Zhang T, Munch K, Denbratt I. An experimental study on the use of butanol or octanol blends in a heavy duty diesel engine. SAE Int J Fuels Lubr 2015;8(3):610–21.
[150] Tornatore C, Marchitto L, Valentino G, Corcione FE, Merola SS. Optical diagnostics of the combustion process in a PFI SI boosted engine fueled with butanol–gasoline blend. Energy 2012;45(1):277–87.
[151] Gu X, Huang Z, Cai J, Gong J, Wu X, Lee C-F. Emission characteristics of a spark-ignition engine fuelled with gasoline-n-butanol blends in combination with EGR. Fuel 2012;93:611–7.
[152] Szwaja S, Naber J. Combustion of n-butanol in a spark-ignition IC engine. Fuel 2010;89(7):1573–82.
[153] Alasfour F. Butanol—a single cylinder engine study: engine performance. Int J Energy Res 1997;21(1):21–30.
[154] Yacoub Y, Bata R, Gautam M. The performance and emission characteristics of C1-C5 alcohol-gasoline blends with matched oxygen content in a single-cylinder spark ignition engine. Proc Inst Mech Eng Part A: J Power Energy 1998;212(5):363–79.
[155] Gautam M, Martin D, Carder D. Emissions characteristics of higher alcohol/gasoline blends. Proc Inst Mech Eng Part A: J Power Energy 2000;214(2):165–82.
[156] Miller G, Smith J, Workman J. Engine performance using butanol fuel blends. Trans ASAE 1981;24(3):538–0540.
[157] Wallner T, Miers SA, McConnell S. A comparison of ethanol and butanol as oxygenates using a direct-injection, spark-ignition engine. J Eng Gas Turbines Power 2009;131(3):032802.
[158] Gautam M, Martin D. Combustion characteristics of higher-alcohol/gasoline blends. Proc Inst Mech Eng Part A: J Power Energy 2000;214(5):497–511.
[159] Irimescu A. Performance and fuel conversion efficiency of a spark ignition engine

fueled with isobutanol. Appl Energy 2012;96:477–83.
[160] Alasfour F. The effect of using 30% isobutanol-gasoline blend on hydrocarbon emissions from a spark-ignition engine. Energy Sources 1999;21(5):379–94.
[161] Alasfour F. NOx emission from a spark ignition engine using 30% isobutanol–gasoline blend: Part 2—ignition timing. Appl Therm Eng 1998;18(8):609–18.
[162] Lujaji F, Bereczky A, Janosi L, Novak C, Mbarawa M. Cetane number and thermal properties of vegetable oil, biodiesel, 1-butanol and diesel blends. J Therm Anal Calorim 2010;102(3):1175–81.
[163] Weerachanchai P, Tangsathitkulchai C, Tangsathitkulchai M. Phase behaviors and fuel properties of bio-oil–diesel–alcohol blends. World Acad Sci Eng Technol 2009;56:387–93.
[164] Yilmaz N, Vigil FM, Benalil K, Davis SM, Calva A. Effect of biodiesel–butanol fuel blends on emissions and performance characteristics of a diesel engine. Fuel 2014;135:46–50.
[165] Makareviciene V, Sendzikiene E, Janulis P. Solubility of multi-component biodiesel fuel systems. Bioresour Technol 2005;96(5):611–6.
[166] Masum B, Masjuki H, Kalam M, Fattah IR, Palash S, Abedin M. Effect of ethanol–gasoline blend on NOx emission in SI engine. Renew Sustain Energy Rev 2013;24:209–22.
[167] Zhao Z, Xu Z, Liu J, Wang M, Lee C-F, Chang W, Hou J. Experimental and numerical investigation of soot mechanism of acetone-butanol-ethanol (ABE) with various oxygen concentrations. SAE International; 2015.
[168] Lin Y, Lee T, Nithyanandan K, Zhang J, Li Y, Lee C-F. Experimental investigation and analysis of combustion process in a diesel engine fueled with acetone-butanol-ethanol/ diesel blends. SAE International; 2016.
[169] Li Y, Meng L, Nithyanandan K, Lee TH, Lin Y, Lee C-fF, Liao S. Combustion, performance and emissions characteristics of a spark-ignition engine fueled with isopropanol-n-butanol-ethanol and gasoline blends. Fuel 2016;184:864–72.
[170] Veloo PS, Wang YL, Egolfopoulos FN, Westbrook CK. A comparative experimental and computational study of methanol, ethanol, and n-butanol flames. Combust Flame 2010;157(10):1989–2004.
[171] Li Q, Cheng Y, Jin W, Chen Z, Huang Z. Study on the laminar characteristics of ethanol, n-butanol and n-pentanol flames. SAE International; 2015.
[172] Li Q, Jin W, Huang Z. Laminar flame characteristics of C1-C5 primary alcohol-isooctane blends at elevated temperature. Energies 2016;9(7):511.
[173] Beeckmann J, Cai L, Pitsch H. Experimental investigation of the laminar burning velocities of methanol, ethanol, n-propanol, and n-butanol at high pressure. Fuel 2014;117:340–50.
[174] Mohamed BM. Burning velocities and flame temperatures of ethanol and butanol-air mixtures. Babylon: Technical Institut; 2009.
[175] Takashi H, Kimitoshi T. Laminar flame speeds of ethanol, n-heptane, iso-octane air mixtures; 2006.
[176] Pichon S, Black G, Chaumeix N, Yahyaoui M, Simmie JM, Curran HJ, Donohue R. The combustion chemistry of a fuel tracer: measured flame speeds and ignition delays and a detailed chemical kinetic model for the oxidation of acetone. Combust Flame 2009;156(2):494–504.
[177] Trindade WRdS, Santos RGd. Review on the characteristics of butanol, its production and use as fuel in internal combustion engines. Renew Sustain Energy Rev 2017;69:642–51.
[178] Li Y, Nithyanandan K, Zhang J, Lee C-F, Liao S. Combustion and emissions performance of a spark ignition engine fueled with water containing acetone-butanol-ethanol and gasoline blends. SAE International; 2015.
[179] Bilgin A, Durgun O, Sahin Z. The effects of diesel-ethanol blends on diesel engine performance. Energy Sources 2002;24(5):431–40.
[180] Ren Y, Huang Z, Jiang D, Li W, Liu B, Wang X. Effects of the addition of ethanol and cetane number improver on the combustion and emission characteristics of a compression ignition engine. Proc Inst Mech Eng Part D: J Automob Eng 2008;222(6):1077–87.
[181] Lü X-C, Yang J-G, Zhang W-G, Huang Z. Improving the combustion and emissions of direct injection compression ignition engines using oxygenated fuel additives combined with a cetane number improver. Energy fuels 2005;19(5):1879–88.
[182] Park SH, Youn IM, Lee CS. Influence of ethanol blends on the combustion performance and exhaust emission characteristics of a four-cylinder diesel engine at various engine loads and injection timings. Fuel 2011;90(2):748–55.
[183] Tsang K, Zhang Z, Cheung C, Chan T. Reducing emissions of a diesel engine using fumigation ethanol and a diesel oxidation catalyst. Energy Fuels 2010;24(11):6156–65.
[184] Surawski NC, Ristovski ZD, Brown RJ, Situ R. Gaseous and particle emissions from an ethanol fumigated compression ignition engine. Energy Convers Manag 2012;54(1):145–51.
[185] Nakata K, Utsumi S, Ota A, Kawatake K, Kawai T, Tsunooka T. The effect of ethanol fuel on a spark ignition engine, SAE Technical Paper; 2006.
[186] Aleiferis P, Serras-Pereira J, Richardson D. Characterisation of flame development with ethanol, butanol, iso-octane, gasoline and methane in a direct-injection spark-ignition engine. Fuel 2013;109:256–78.
[187] Türköz N, Erkuş B, İhsan Karamangil M, Sürmen A, Arslanoğlu N. Experimental investigation of the effect of E85 on engine performance and emissions under various ignition timings. Fuel 2014;115:826–32.
[188] Costagliola M, De Simio L, Iannaccone S, Prati M. Combustion efficiency and engine out emissions of a SI engine fueled with alcohol/gasoline blends. Appl Energy 2013;111:1162–71.
[189] Koç M, Sekmen Y, Topgül T, Yücesu HS. The effects of ethanol–unleaded gasoline blends on engine performance and exhaust emissions in a spark-ignition engine. Renew Energy 2009;34(10):2101–6.
[190] Cooney CP, Worm JJ, Naber JD. Combustion characterization in an internal combustion engine with ethanol–gasoline blended fuels varying compression ratios and ignition timing. Energy Fuels 2009;23(5):2319–24.
[191] Yücesu HS, Topgül T, Cinar C, Okur M. Effect of ethanol–gasoline blends on engine performance and exhaust emissions in different compression ratios. Appl Therm Eng 2006;26(17):2272–8.
[192] Durbin TD, Miller J, Younglove T, Huai T, Cocker K. Effects of ethanol and volatility parameters on exhaust emissions. CRC Project No. E-67; 2006.
[193] Eyidogan M, Ozsezen AN, Canakci M, Turkcan A. Impact of alcohol–gasoline fuel blends on the performance and combustion characteristics of an SI engine. Fuel 2010;89(10):2713–20.
[194] Bielaczyc P, Szczotka A, Woodburn J. A study of gasoline-ethanol blends influence on performance and exhaust emissions from a light-duty gasoline engine. SAE International; 2012.
[195] Sharma G, Lal H. Effects of ethanol-gasoline blends on engine performance and exhaust emissions in a spark ignition. Int J Emerg Technol 2015;6(2):184.
[196] Varde K, Clark CP. A comparison of burn characteristics and exhaust emissions from off-highway engines fueled by EO and E85. In: Proceedings of the third international conference on automotive and fuel technology. Allied Publishers; 2004.
[197] Al-Hasan M. Effect of ethanol–unleaded gasoline blends on engine performance and exhaust emission. Energy Convers Manag 2003;44(9):1547–61.
[198] Aikawa K, Sakurai T, Hayashi A. Study of ethanol-blended fuel (E85) effects under cold-start conditions. SAE Int J Fuels Lubr 2009;2(1):196–203.
[199] Graham LA, Belisle SL, Baas C-L. Emissions from light duty gasoline vehicles operating on low blend ethanol gasoline and E85. Atmos Environ 2008;42(19):4498–516.
[200] Bielaczyc P, Szczotka A, Woodburn J. The effect of various petrol-ethanol blends on exhaust emissions and fuel consumption of an unmodified light-duty SI vehicle. SAE International; 2011.
[201] Sward K. The legend of Henry Ford Rinehart. New York; 1948.
[202] Shahad HA, Wabdan SK. Effect of operating conditions on pollutants concentration emitted from a spark ignition engine fueled with gasoline bioethanol blends. J Renew Energy 2015;2015:1–7.
[203] Karavalakis G, Short D, Vu D, Villela M, Russell R, Jung H, Asa-Awuku A, Durbin T. Regulated emissions, air toxics, and particle emissions from SI-DI light-Duty vehicles operating on different Iso-butanol and ethanol blends. SAE Int J Fuels Lubr 2014;7(1):183–99.
[204] Grana R, Frassoldati A, Faravelli T, Niemann U, Ranzi E, Seiser R, Cattolica R, Seshadri K. An experimental and kinetic modeling study of combustion of isomers of butanol. Combust Flame 2010;157(11):2137–54.
[205] Veloo PS, Egolfopoulos FN. Flame propagation of butanol isomers/air mixtures. Proc Combust Inst 2011;33(1):987–93.
[206] Gu X, Huang Z, Li Q, Tang C. Measurements of laminar burning velocities and Markstein lengths of n-butanol− air premixed mixtures at elevated temperatures and pressures. Energy Fuels 2009;23(10):4900–7.
[207] Gu X, Huang Z, Wu S, Li Q. Laminar burning velocities and flame instabilities of butanol isomers–air mixtures. Combust Flame 2010;157(12):2318–25.
[208] Wu F, Law CK. An experimental and mechanistic study on the laminar flame speed, Markstein length and flame chemistry of the butanol isomers. Combust Flame 2013;160(12):2744–56.
[209] Gu X, Li Q, Huang Z. Laminar burning characteristics of diluted n-butanol/air mixtures. Combust Sci Technol 2011;183(12):1360–75.
[210] Sarathy SM, Thomson MJ, Togbé C, Dagaut P, Halter F, Mounaim-Rousselle C. An experimental and kinetic modeling study of n-butanol combustion. Combust Flame 2009;156(4):852–64.
[211] Pan L, Zhang Y, Tian Z, Yang F, Huang Z. Experimental and kinetic study on ignition delay times of isobutanol. Energy Fuels 2014;28(3):2160–9.
[212] Zhang J, Niu S, Zhang Y, Tang C, Jiang X, Hu E, Huang Z. Experimental and modeling study of the auto-ignition of n-heptane/n-butanol mixtures. Combust Flame 2013;160(1):31–9.
[213] Zhang J, Wei L, Man X, Jiang X, Zhang Y, Hu E, Huang Z. Experimental and modeling study of n-butanol oxidation at high temperature. Energy Fuels 2012;26(6):3368–80.
[214] Black G, Curran HJ, Pichon S, Simmie JM, Zhukov V. Bio-butanol: combustion properties and detailed chemical kinetic model. Combust Flame 2010;157(2):363–73.
[215] Weber BW, Kumar K, Zhang Y, Sung C-J. Autoignition of n-butanol at elevated pressure and low-to-intermediate temperature. Combust Flame 2011;158(5):809–19.
[216] Moss JT, Berkowitz AM, Oehlschlaeger MA, Biet J, Warth V, Glaude P-A, Battin-Leclerc F. An experimental and kinetic modeling study of the oxidation of the four isomers of butanol. J Phys Chem A 2008;112(43):10843–55.
[217] Chang Y-C, Lee W-J, Lin S-L, Wang L-C. Green energy: water-containing acetone–butanol–ethanol diesel blends fueled in diesel engines. Appl Energy 2013;109:182–91.
[218] Farrell J, Johnston R, Androulakis I. Molecular structure effects on laminar burning velocities at elevated temperature and pressure. SAE Pap 2004;1:2936–58.
[219] Wigg B, Coverdill R, Lee C-F, Kyritsis D. Emissions characteristics of neat butanol fuel using a port fuel-injected, spark-ignition engine, SAE Technical Paper; 2011.
[220] Pechout M, Mazac M, Vojtisek-Lom M. Effect of higher content n-butanol blends on combustion, exhaust emissions and catalyst performance of an unmodified SI vehicle engine. SAE International; 2012.
[221] Dernotte J, Mounaim-Rousselle C, Halter F, Seers P. Evaluation of butanol–gasoline blends in a port fuel-injection, spark-ignition engine. Oil Gas Sci Technol l'Institut Fr Pétrole 2010;65(2):345–51.

[222] Chang Y-C, Lee W-J, Wu TS, Wu C-Y, Chen S-J. Use of water containing acetone–butanol–ethanol for NOx-PM (nitrogen oxide-particulate matter) trade-off in the diesel engine fueled with biodiesel. Energy 2014;64:678–87.

[223] Lee TH, Lin Y, Wu H, Meng L, Hansen A, Lee C-F. Characterization spray and combustion processes of acetone-butanol-ethanol (ABE) in a constant volume chamber, SAE Technical Paper; 2015.

[224] Lin Y, Wu H, Nithyanandan K, Lee TH, Chia-fon FL, Zhang C. Investigation of high percentage acetone-butanol-ethanol (ABE) blended with diesel in a constant volume chamber. In: Proceedings of ASME 2014 internal combustion engine division fall technical conference. American Society of Mechanical Engineers; 2014.

[225] Zhang S, Xu Z, Lee T, Lin Y, Wu W, Lee C-F. A semi-detailed chemical kinetic mechanism of acetone-butanol-ethanol (ABE) and diesel blends for combustion simulations. SAE Int J Engines 2016;9(1):631–40.

[226] Wu H, Nithyanandan K, Zhang J, Lin Y, Lee TH, Lee C, Zhang C. Impacts of acetone–butanol–ethanol (ABE) ratio on spray and combustion characteristics of ABE–diesel blends. Appl Energy 2015;149:367–78.

[227] Gong J, Zhang S, Cheng Y, Huang Z, Tang C, Zhang J. A comparative study of n-propanol, propanol, acetone, and propane combustion in laminar flames. Proc Combust Inst 2015;35(1):795–801.

[228] Burluka AA, Harker M, Osman H, Sheppard CGW, Konnov AA. Laminar burning velocities of three C3H6O isomers at atmospheric pressure. Fuel 2010;89(10):2864–72.

[229] Wu H, Nithyanandan K, Zhou N, Lee TH, Lee C-fF, Zhang C. Impacts of acetone on the spray combustion of Acetone–butanol–ethanol (ABE)-diesel blends under low ambient temperature. Fuel 2015;142:109–16.

[230] Van Geem KM, Cuoci A, Frassoldati A, Pyl SP, Marin GB, Ranzi E. An experimental and kinetic modeling study of pyrolysis and combustion of acetone–butanol–ethanol (ABE) mixtures. Combust Sci Technol 2012;184(7–8):942–55.

[231] Wu H, Nithyanandan K, Lee TH, Lee C-fF, Zhang C. Spray and combustion characteristics of neat acetone-butanol-ethanol, n-butanol, and diesel in a constant volume chamber. Energy Fuels 2014;28(10):6380–91.

[232] Zhou N, Huo M, Wu H, Nithyanandan K, Lee C-fF, Wang Q. Low temperature spray combustion of acetone–butanol–ethanol (ABE) and diesel blends. Appl Energy 2014;117:104–15.

[233] Ma X, Zhang F, Han K, Yang B, Song G. Evaporation characteristics of acetone–butanol–ethanol and diesel blends droplets at high ambient temperatures. Fuel 2015;160:43–9.

[234] Wu H, Lee TH, Lee C-F, Liu F, Sun B. Optical soot measurement of bio-butanol upstream product, ABE (acetone–Butanol–ethanol), under diesel-like conditions. Fuel 2016;181:300–9.

[235] Nithyanandan K, Wu H, Huo M, Lee C-F. A Preliminary Investigation Of The Performance And Emissions Of A Port-fuel Injected SI Engine Fueled With Acetone-butanol-ethanol (ABE) and gasoline. SAE Pap 2014:01–1459.

[236] Nithyanandan K, Chia-fon FL, Wu H, Zhang J. Performance and Emissions Of Acetone-butanol-ethanol (ABE) and gasoline blends in a port fuel injected spark ignition engine. In: Proceedings of ASME 2014 internal combustion engine division fall technical conference. American Society of Mechanical Engineers; 2014.

[237] Li Y, Nithyanandan K, Lee TH, Donahue RM, Lin Y, Lee C-F, Liao S. Effect of water-containing acetone–butanol–ethanol gasoline blends on combustion, performance, and emissions characteristics of a spark-ignition engine. Energy Convers Manag 2016;117:21–30.

[238] Zhang J, Nithyanandan K, Li Y, Lee C-F, Huang Z. Comparative study of high-alcohol-content gasoline blends in an SI engine. SAE International; 2015.

[239] Nithyanandan K, Zhang J, Li Y, Wu H, Lee TH, Lin Y, Lee C-fF. Improved SI engine efficiency using acetone–butanol–ethanol (ABE). Fuel 2016;174:333–43.

[240] Rao DCK, Karmakar S, Som SK. Puffing and micro-explosion behavior in combustion of butanol/jet A-1 and acetone-butanol-ethanol (A-B-E)/jet A-1 fuel droplets. Combust Sci Technol 2017:1–17.

2.2 Summary of Article I

Article I concluded that using ABE as an intermediate blend of butanol resulted in significant cost reduction. Also, including acetone in the ABE blend has some benefits: improving vaporisation and advancing combustion, which result in an increased reaction rate. This consequently improves engine performance such as thermal efficiency; and reduces engine emissions such as NO_x, CO, soot emission and combustion temperature.

Experimental studies using ethanol as an additive to diesel have found some drawbacks such as corrosion behaviour in the fuel injection system. Therefore, using another blend such as a BA blend with a ratio of 2.9:1 (Li et al. 2014) without ethanol and with a high butanol content could be a good additive to diesel fuel.

The literature addressed the gap that needs to be filled:

- There is a lack of studies related to spray characteristics of butanol-diesel blend, ABE-diesel blend, BA-diesel and BA-biodiesel blend for various blend ratios and operating conditions.
- There is a lack of studies related to engine performance using BA-diesel blend.
- There are limited studies testing and comparing spray characteristics and engine performance using n-BA or iso-BA-diesel blend.
- There is a lack of studies related to engine performance using a dual blend of n-butanol-iso-butanol with diesel.
- There is a lack of studies related to spray characteristics and engine performance using a BA-biodiesel blend.
- There are very few studies regarding the low purity of BA blends tested in CI or SI engines.

Through this investigation into spray characteristics, efficient diesel engine performance can be achieved by controlling injection characteristics, especially when using a renewable additive blended with diesel.

Chapter 3 - Spray Behaviour of Butanol-Diesel Blends

3.1 Article II

Algayyim, S. J. M, Wandel, A. P., and Yusaf, T., The Impact of Injector Hole Diameter on Spray Behaviour of Butanol-Diesel Blends. *Energies*, 2018. 11(5): p. 1298.

Article II (Chapter 3) investigates the spray characteristics of bio-alcohol under various blend ratios and operating conditions. Spray tests were carried out in a CVV under different injection conditions (injector hole diameter, injection pressure, and injection durations). A high-speed camera was used to record spray images. Macroscopic spray characteristics (spray penetration, spray cone angle and spray volume) were calculated and measured.

energies

MDPI

Article

The Impact of Injector Hole Diameter on Spray Behaviour for Butanol-Diesel Blends

Sattar Jabbar Murad Algayyim [1,2,*], Andrew P. Wandel [1] and Talal Yusaf [1]

[1] School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba 4350, QLD, Australia; andrew.wandel@usq.edu.au (A.P.W.); Talal.Yusaf@usq.edu.au (T.Y.)

[2] Department of Mechanical, College of Engineering, University of Al-Qadisiyah, Al-Diwaniyah 58001, Iraq

* Correspondence: sattarjabbarmurad.algayyim@usq.edu.au or ialiraq12@yahoo.com; Tel.: +61-431-291-580

Received: 6 April 2018; Accepted: 10 May 2018; Published: 19 May 2018

Abstract: Optimising the combustion process in compression ignition (CI) engines is of interest in current research as a potential means to reduce fuel consumption and emission levels. Combustion optimisation can be achieved as a result of understanding the relationship between spraying technique and combustion characteristics. Understanding macroscopic characteristics of spray is an important step in predicting combustion behaviour. This study investigates the impact of injector hole diameter on macroscopic spray characteristics (spray penetration, spray cone angle, and spray volume) of butanol-diesel blends. In the current study, a Bosch (0.18 mm diameter) and a Delphi (0.198 mm) injector were used. Spray tests were carried out in a constant volume vessel (CVV) under different injection conditions. The test blends were injected using a solenoid injector with a common rail injection system and images captured using a high-speed camera. The experimental results showed that the spray penetration (S) was increased with larger hole diameter. Spray penetration of a 20% butanol-80% diesel blend was slightly further than that of neat diesel. Spray penetration of all test fuels was increased as a result of increased injection pressure (IP), while spray cone angle (θ) was slightly widened due to the increase in either hole diameter or injection pressure. Spray volume of all test fuels was increased as a result of increased hole diameter or injection pressure. Thus, an efficient diesel engine performance can be achieved as a result of controlling injection characteristics, especially when using a promising additive like butanol blended with diesel.

Keywords: butanol; spray characteristics; injector hole diameter; visualisation

---

1. Introduction

As a response to the high demand for environmental security, more attention is being paid to utilising fuels with lower emissions and optimising combustion processes [1–8]. Optimising the combustion process in compression ignition (CI) engines has been employed in the current study because this can reduce fuel consumption and pollutants [9–13]. Combustion optimisation can be achieved through an understanding of spray behaviour in CI engines [13]. CI engines' performance and emissions are very sensitive to fuel spray behaviour (controlled by the nozzle geometry; the nozzle position in engine cylinder; and the injection method, such as direct injection or dual injection), which influence fuel-air surface area contact and mixing rate. Visualisation techniques are sometimes applied in engine configurations with optical access [14,15] (using either a modified or a specially-built engine). Alternatively, a constant volume vessel (CVV) can be used at either similar conditions to real engines [16–19] or at atmospheric conditions [20,21] because design and fabrication of an engine with an optical window is a costly and complex option [22–24].

Another mechanism to reduce environmental impact is to utilise one of the growing number of alternative fuels such as alcohols [1–3] or biodiesel [25]. This has led to increased and accelerated interest in studying the relationship between spray techniques and combustion characteristics of these fuels [21]. Butanol has become an important alternative fuel for CI engines in recent years due to its eco-friendly production method [2,26]. It also has favourable physicochemical properties compared to ethanol [1,27–34]: it is less hygroscopic, reducing corrosion in the fuel injection system [27]; and it is safer in fuel tanks and storage because of its higher flash point. Furthermore, the lower viscosity, higher laminar flame speed and oxygen content of butanol [28,30] compared to neat diesel result in an enhanced atomization, vaporization and reaction rate, which produce emissions (such as soot, smoke, NO_x and CO) reductions CI engines [29–34].

Some previous studies have investigated the impact of butanol as an additive on characteristic spray behaviour. Liu et al. [35] compared the effects of 20% ethanol and 20% butanol as additives in 80% soybean biodiesel fuel (B20S80 and E20S80, respectively) using a CVV at different ambient temperatures from 800 to 1200 K. Both ethanol and butanol blends enhance the spray behaviour of biodiesel due to improving biodiesel properties such as viscosity and surface tension. Wu et al. [36] examined the effect of *n*-butanol (B) and an acetone-butanol-ethanol (ABE) mixture on spray behaviour under different temperatures and oxygen content in a CVV. The images of the experimental results showed that liquid penetrations of B and the ABE mixture were much shorter than that of neat diesel under high ambient temperatures. Both neat B and ABE have a lower boiling point, lower viscosity and higher vapour pressure compared to neat diesel, which improves the vaporisation and atomisation rate. Rao et al. [37] investigated the droplets fragmentation behaviour of three blend ratios (10%, 30% and 50%) of B and ABE blended with jet A-1 fuel. The fragmentation of droplets plays a major factor in increasing atomization and vaporization rate, which can lead to efficient combustion. Algayyim et al. [8] experimentally and numerically investigated macroscopic and microscopic spray characteristics of butanol-diesel blends under different ambient conditions. They found that a butanol blend can enhance spray characteristics such as spray tip penetration.

Spray parameters are also affected by spray injection pressure and injector geometry (hole diameter, number of holes, and spray angle). A higher injection pressure (IP) enhances the interaction between ambient gases and droplets as a result of higher kinetic energy [12,22,38]. The turbulent and cavitation characteristics of an injector can be directly affected by the nozzle geometry and position [11,39–41]. Moon et al. [41] investigated the effect of the number (1, 3 and 6) nozzle holes with nozzle hole diameter 0.12 mm on the dynamic characteristics of diesel injection. They found that the multi-hole injector significantly alters the flow patterns of the injected fuel compared to the single-hole injector, which results in more mixing rate between injected fuel and available air.

Some research has been conducted into the spray characteristics resulting from realistic diesel multi-hole nozzles with different hole diameters [42,43]. Mulemane et al. [42] experimentally and numerically investigated the effect of injection pressure and injector hole diameter on injection rate and, consequently, spray characteristics. Lai et al. [43] also experimentally studied the impact of the injector geometry features such as nozzle shape, needle lift, and injection pressure on fuel spray characteristics, with the spray behaviour near the nozzle tip strongly dependent on nozzle geometry. Kuti et al. [44] examined the effect of two injection hole diameters (0.08 and 0.16 mm) on spray evaporation of neat biodiesel and neat conventional diesel under 100 MPa and 300 MPa injection pressures. The experimental results showed that the ignition region was bigger for the larger hole diameter, while it was smaller as a result of increased injection pressure.

This work expands current knowledge by investigating the impact of injector hole diameter and injection pressure on spray penetration, spray cone angle and spray volume of butanol-diesel blends.

2. Fuel Preparation and Properties

Analytical grade normal butanol (B, 99.8%) supplied from Chem Supply Australia (Adelaide, Australia) was used. Conventional diesel supplied from a local Caltex petrol station in Toowoomba (Australia) was used as a baseline. 20% butanol (B) was blended with 80% neat diesel, referred to as B20D80. The density was measured for all test fuel blends according to ASTM 1298 [3]. The dynamic viscosities of the test fuels were measured according to the ASTM 445-01 [1] fuel standards by using a Brookfield Viscometer (DV-II+Pro Extra, AMETEK Brookfield, Middleboro, MA, USA); then the kinematic viscosity was subsequently calculated. The calorific values of the test blends were measured using a digital oxygen bomb calorimeter (XRY-1A, Shanghai Changji Geological Instrument Co., Ltd., Shanghai, China) following ASTM D240 [1,3]. Fuel properties of the test fuel blends are listed in Table 1.

Table 1. Properties of the test fuel blends.

Properties	Diesel (D)	Butanol (B)	B20D80
Chemical formula	C_{12}–C_{25}	C_4H_9OH	-
Composition (C, H, O) (mass %)	-	65, 13.5, 21.5	-
Density (kg/L)	0.86 [a]	0.810 [b]	0.825 [a]
Viscosity (mm^2/s) at 40 °C	2.46 [a]	2.2 [b]	2.25 [a]
Calorific value (MJ/kg)	42.65 [a]	33.1 [b]	41.17 [a]
Surface tension (mN/m)	23.8 [b]	24.2 [b]	-
Cetane number	48 [b]	17–25 [b]	-
Latent heat of vaporisation (kJ/kg)	270 [b]	582 [b]	-
Boiling point (°C)	200–400 [b]	118 [b]	-
Flash point (°C)	74 [b]	35 [b]	-

[a]: Properties are measured; [b]: Properties are from [1,2].

3. Experimental Setup and Procedure

3.1. Spray Test Setup

Figures 1 and 2 show the schematic of the experimental system setup. A high-pressure common-rail injection system was used to inject the test fuels into the CVV through a solenoid 6-hole injector, either a Bosch injector (part#: 0 445 110 107, Robert Bosch, Gerlingen, Germany) with 0.18 mm diameter holes or a Delphi injector (SH0.135/SH0.096, Delphi Technologies, Troy, MI, USA) with 0.198 mm diameter holes. Both injectors have the same enclosed angle (156°) which means the identical characteristics of both injectors was employed except orifice diameter. Figure 3 shows the solenoid injector diagram including the hole diameter of both the Bosch and Delphi injectors. More detailed specifications of the injectors, visual data acquisition system and injection setup are listed in Table 2.

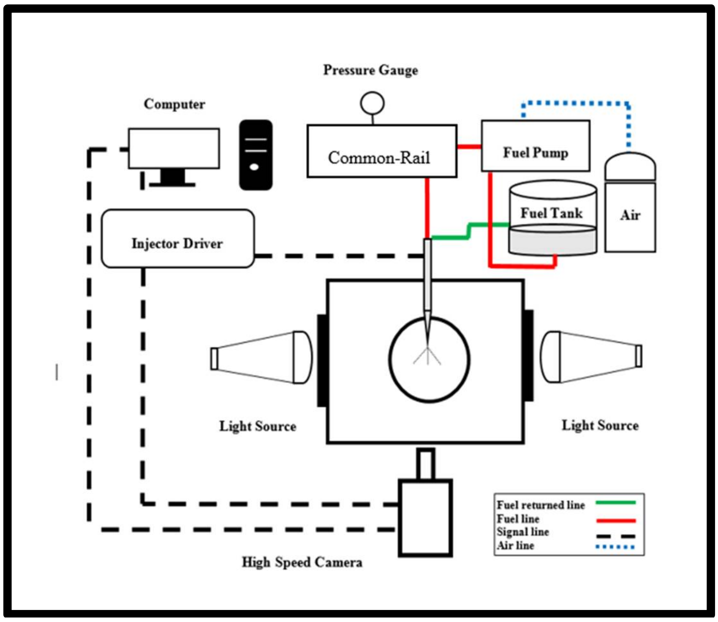


Figure 1. Schematic of the constant volume vessel with common rail fuel injection system setup, light source and visual data acquisition system.

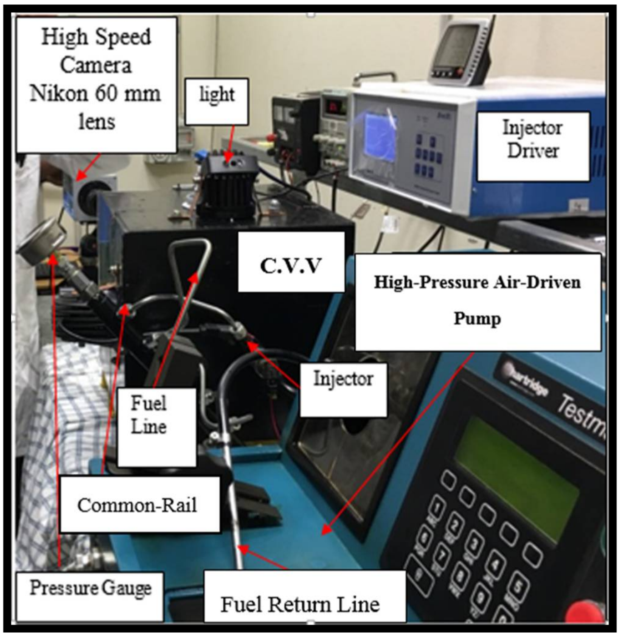


Figure 2. Experimental setup.

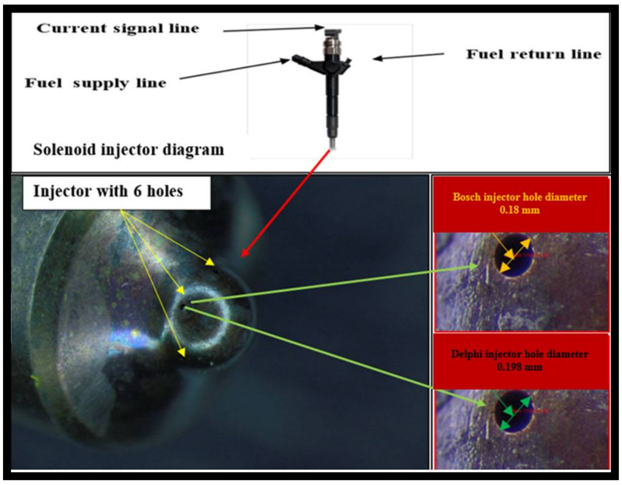


Figure 3. Solenoid injector diagram including hole diameter of Bosch and Delphi injectors.

Table 2. Specifications of the injector, high-speed camera and injection setup.

Injector Make/Type	
Injector type	Bosch electromagnetic common rail solenoid injector (hole diameter 0.18 mm)
	Delphi electromagnetic common rail solenoid injector (hole diameter 0.198 mm)
Injection enclosed angle	156°
Number of injector holes	6
Injection quantity	12 mg
Camera Specification and Filter	
Camera resolution at frame rate	1024 × 1024 pixels at 2000 fps
Filter size	62 mm
Injection Setup	
Injection pressure	300 & 500 bar
After start of injection time (ASOI)	0.5, 0.75, 1 and 1.5 ms
Fuel temperature	21.5 °C
Room temperature	22.8 °C

A SA3 high-speed camera (Photron, Tokyo, Japan) with a resolution of 1024 × 1024 pixels, connected with a Nikon lens (Nikon Corporation, Tokyo, Japan) and filter size 62 mm, was used to capture the images of the spray test blends. The shutter speed and frame rate were fixed at 1/2000 frames per second (fps). The CVV was using LED light on each of three windows.

3.2. Spray Test Conditions

The injection quantity was measured by injecting fuel 50 times from a measuring cylinder with the weight of the cylinder measured before and after the 50 injections for each injector. The spray characteristics of the B20D80 blend was investigated and compared to those of neat diesel as a baseline. The amount of butanol in the fuel was limited to 20% in this study so that the diesel engine did not require any modifications. The tests were carried out at atmospheric conditions at the conditions listed in Table 2 in triplicate to ensure accurate results. First, the fuel tank was emptied, cleaned and dried by air compressor for each new blend test. Then the fuel injection system (including common rail and fuel line fittings) were also emptied, cleaned and dried. Furthermore, the fuel filter from each test was removed and replaced with a new one and the spray testing started with a number of initial injections before the new images were captured. Finally, for each spray test, three shots were conducted, with the six plumes for all shots averaged to calculate the spray characteristics. The same elapsed time, injection pressure, and injection environment conditions were maintained for each injector to obtain a good, accurate comparative.

The image processing flow chart is displayed in Figure 4. The images were processed in three steps to enable quantification of the spray characteristics using a similar method to [2,44,45]. Firstly, the images were read in MATLAB (R2015b, The MathWorks, Inc., Natick, MA, USA), then converted into binary images to subtract the initial image thereby removing background effects. An automatic threshold calculation algorithm was employed to determine the spray outline (edge) from the binary images. Finally, the boundary pixels of each spray plume were identified so the spray characteristics (spray penetration, S, and spray cone angle, θ, Figure 5) could be quantified from the spray contour. The fuel spray is assumed to be a cone with a hemisphere [2,46,47] and the spray volume (V in mm^3) is calculated by [44,45]:

$$V = \left(\frac{\pi}{3}\right) S^3 \left[\tan^2(\theta)\right] \frac{1 + 2\tan\left(\frac{\theta}{2}\right)}{\left[1 + \tan\left(\frac{\theta}{2}\right)\right]^3} \tag{1}$$

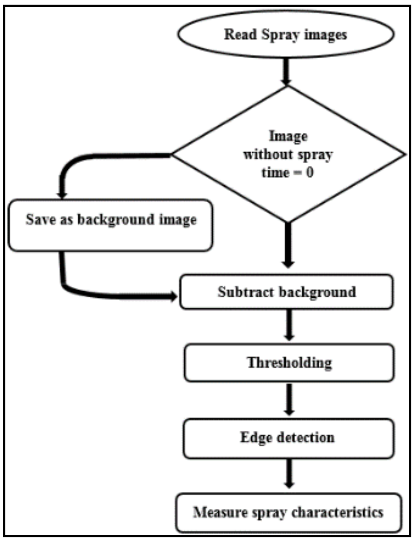


Figure 4. Image processing flowchart.

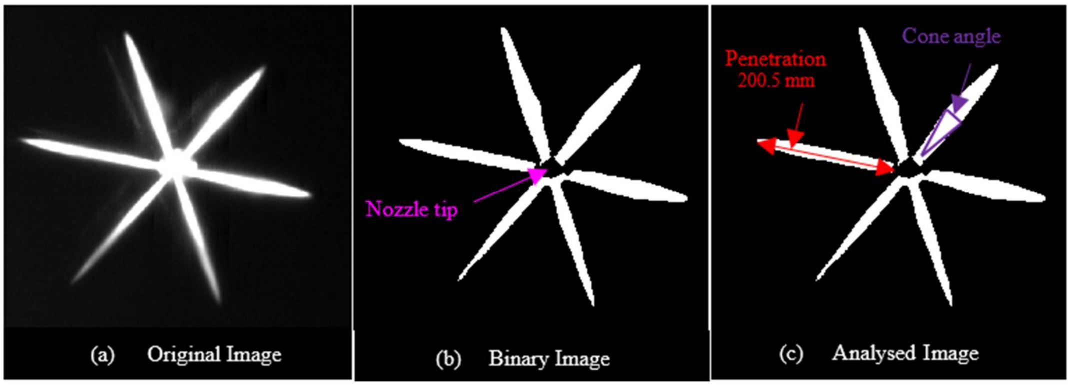


Figure 5. Spray image processing methodology, and spray penetration and spray cone angle definitions. (**a**) Original Image; (**b**) Binary Image; (**c**) Analysed Image.

4. Results of Spray Characteristics and Discussion

4.1. Spray Tip Penetration (S)

The spray evolution and development of all test fuels under all conditions are displayed in Figure 6. These images are samples of triplicate tests. The left side of the figure shows images using the Bosch injector with a hole diameter of 0.18 mm and the right side shows images using the Delphi injector with a hole diameter of 0.198 mm at two injection pressures (IP). Rows from top to bottom show ASOI. The scaling of spray images or spray pattern body became bigger as a result of increased injector hole diameter, ASOI and IP values. Also, the butanol-diesel blend showed some improvement in spray plumes. Spray images of conventional diesel fuel were used as a baseline. The spray characteristics were quantified from these images.

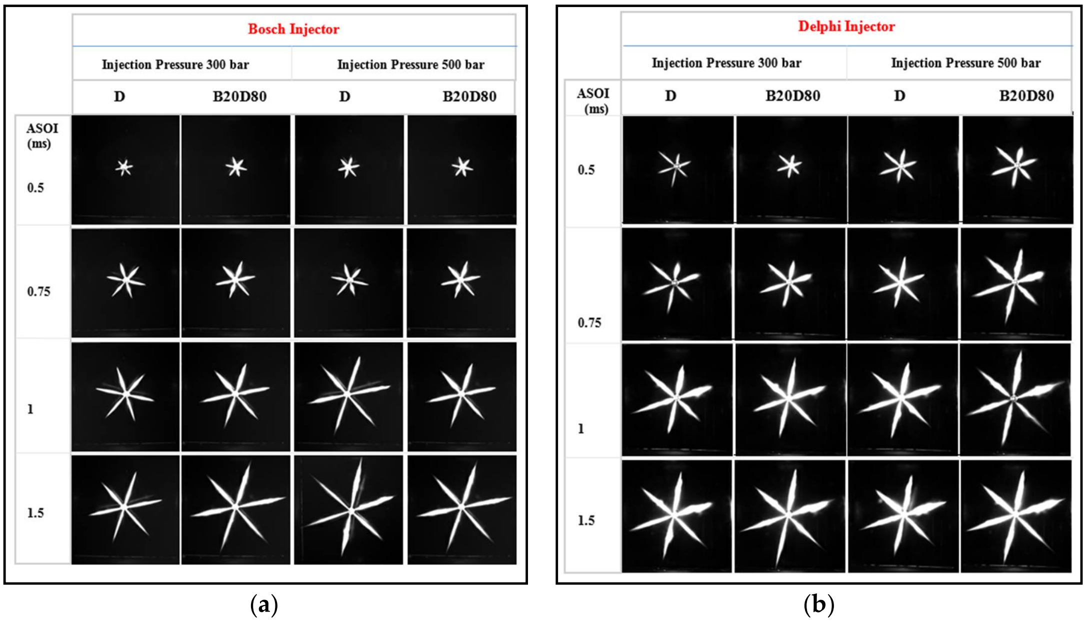
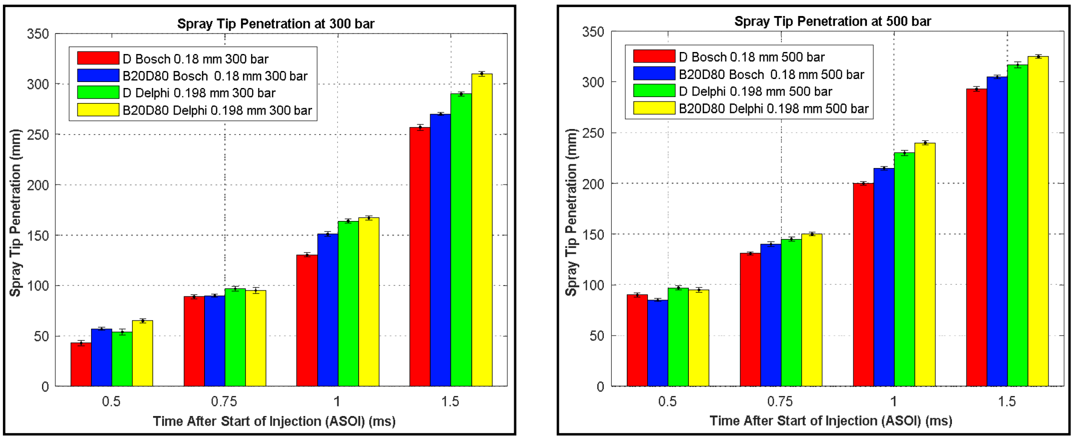


Figure 6. Spray images of test fuels using Bosch injector with hole diameter 0.18 mm (**a**) and Delphi injector with hole diameter 0.198 mm (**b**) at two injection pressures.

Figure 7 compares the effect of hole diameter on spray tip penetration of D and B20D80 blends. Spray tip penetration of the injector with a hole diameter of 0.198 mm produced higher spray tip penetration compared to the injector with a hole diameter of 0.18 mm at the same ASOI, injection pressures and fuel tests. Similar results were reported in [44,45,48]. Cavitation is increased as a result of increased injector hole diameter for internal flow [12], consequently increasing spray penetration. Longer penetration into CI engines together with high swirl ratio and hot walls result in more efficient combustion. However, sometimes (depending on the cylinder and piston geometries) high spray penetration causes unwanted fuel contact on the cylinder walls of compression ignition diesel engines, resulting in lower fuel/air mixing rates, which produces high emissions [49].

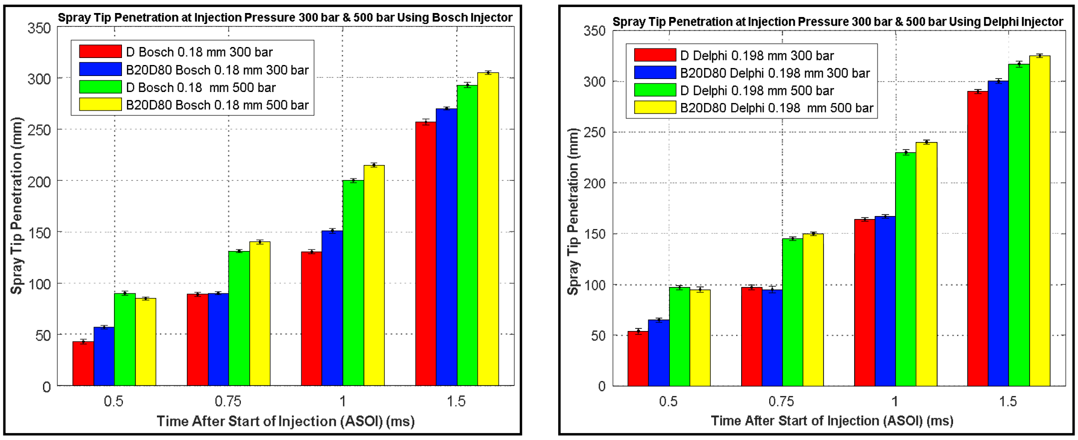


(**a**) (**b**)

Figure 7. Spray tip penetration of test fuels for Bosch and Delphi injectors at two injection pressures. (**a**) Spray tip penetration at 300 bar; (**b**) Spray tip penetration at 500 bar.

Moreover, the injection velocity is reduced with increased hole diameter, which improves the spray break up and mixing rate. However, jet velocities which are too low cause the droplet size to become larger than the nozzle hole diameter because of surface wave fluctuations resulting from surface tension effects, reducing the spray atomisation rate and evaporation speed [12]. Therefore, there is insufficient time to complete the reaction. A high spray velocity is beneficial because it leads to early breakup in the atomisation regime of the nozzle jet, thereby creating smaller spray droplets than the injector's hole diameter.

Spray penetration of B20D80 blend shows a slightly higher value compared to that of neat diesel because the butanol content enhances the diesel properties (viscosity and surface tension), which result in high injection velocity and reduced nozzle loss. Spray tip penetration of test fuel under 500 bar injection pressure also became longer compared to 300 bar injection pressure (Figure 8) because of the higher kinetic energy [12,22]. These results are in agreement with the results reported in [42,49].

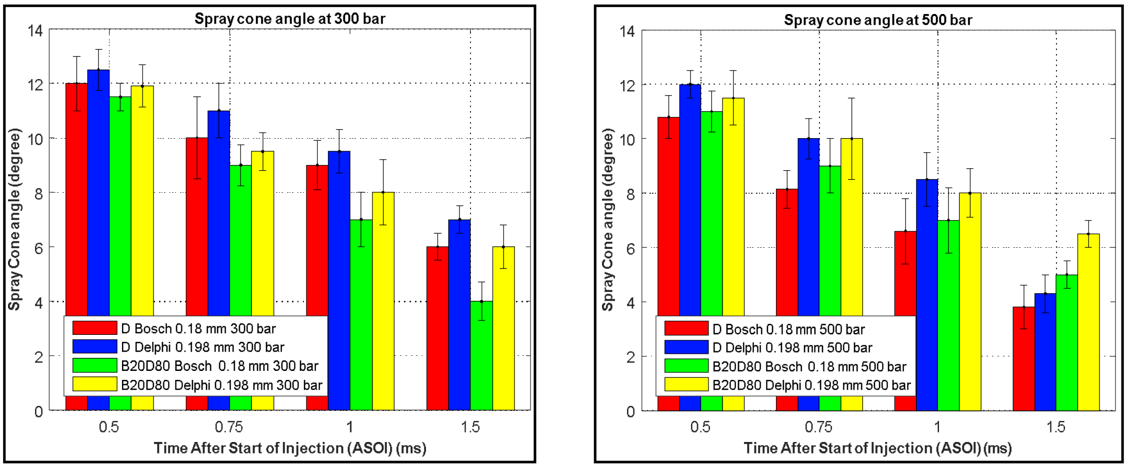


(**a**) (**b**)

Figure 8. Effect of injection pressures (300 to 500 bar) on spray tip penetration of test fuels of Bosch injector (**a**) and Delphi injector (**b**).

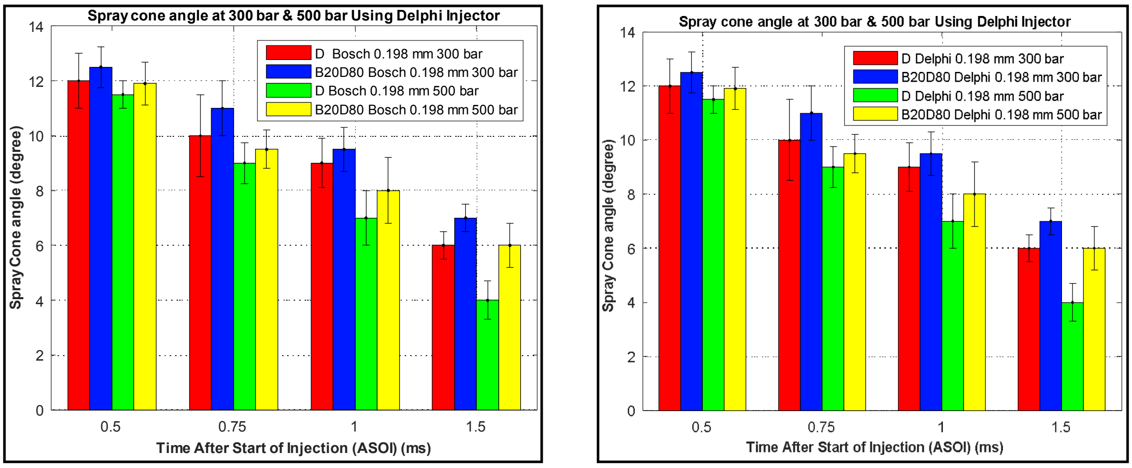
4.2. Spray Cone Angle (θ)

The spray cone angle of the test blends is presented in Figure 9 at two injection pressures for the two different injectors. The spray cone angle was slightly widened for the larger hole diameter (Figure 9), while it was slightly narrowed for the higher injection pressure (Figure 10). Moreover, the spray cone angle was slightly changed for the butanol-diesel blend. Because of the greater uncertainty in determining spray cone angle, it can be stated that there is no significant impact of injector hole diameter, injection pressure and fuel type. However, when there is an insufficient radial momentum to overcome penetration resistance and the pressure difference across the sheet, then spray shoulders become strongly curved. The result was consistent with findings in [1,49].



(**a**) (**b**)

Figure 9. Comparative of effect of two injectors on spray cone angle of test fuel blends. (**a**) Spray cone angle at 300 bar; (**b**) Spray cone angle at 500 bar.

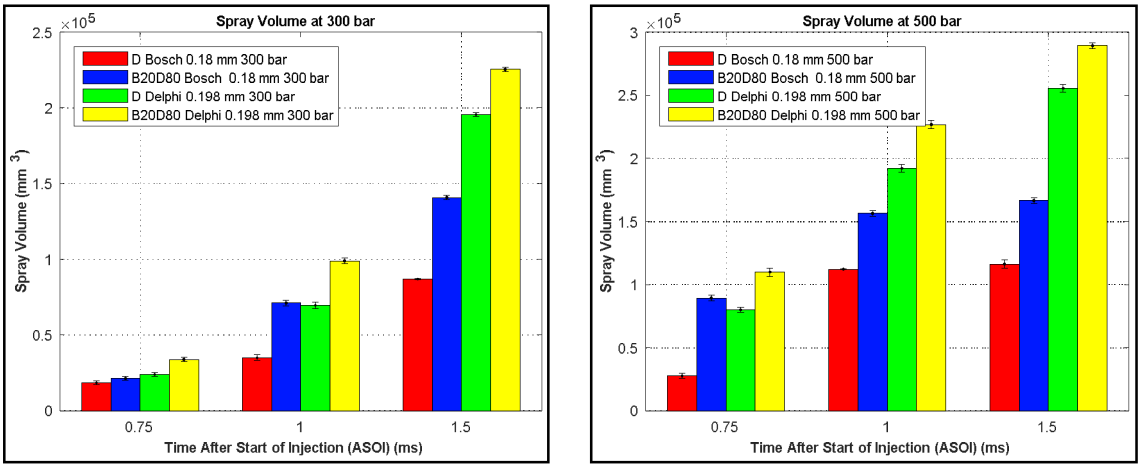


(**a**) (**b**)

Figure 10. Comparative of effect of two injection pressures on spray cone angle of test fuel blends of Bosch injector (**a**) and Delphi (**b**).

4.3. Spray Volume

The spray volume of the test blends is presented in Figure 11 at two injection pressures for the two different injectors. The fuel spray is assumed to be a cone and hemisphere and the spray volume (V) was calculated using Equation 1 for different injection conditions. The spray volume of the test fuel blends increased with larger injector hole diameter or injection pressure because of increased spray penetration. The spray volume of neat diesel was the smallest due to smaller spray penetration and spray cone angle, while the spray volume of the butanol-diesel blend was larger than neat diesel. The spray volume is mainly calculated by the spray penetration length, since the spray cone angles variation among different fuels is not significant, according to these results in Figure 11. Therefore, the contact surface area between the air and fuel would be increased, thereby resulting in increased mixing and reaction rates.



(**a**) (**b**)

Figure 11. Spray volume of test fuels for Bosch and Delphi injectors at two injection pressures. (**a**) Spray volume at 300 bar; (**b**) Spray volume at 500 bar.

5. Conclusions

The experiments studied here revealed the behaviour of the test fuel blends relating to spray evaluation. The spray test was carried out in a constant volume vessel using two multiple hole injectors (hole diameters of 0.18 mm and 0.198 mm). The spray images of the test fuel blends were captured using a high-speed camera and then spray characteristics were measured. Some conclusions follow:

- ❖ The spray images evaluation showed that the spray penetration length was increased with larger hole diameter and high injection pressure. The spray penetration of the B20D80 blend was slightly further than neat diesel because the butanol reduces the viscosity.
- ❖ The spray penetration of the test fuel blends becomes longer while the spray cone angle was slightly widened via the increase in either injection pressure or hole diameter.
- ❖ The spray volume of all the test fuels was increased as a result of increased hole diameter or injection pressures, which results in increased contact surface area between air and fuel, thereby resulting in increased mixing rate and combustion efficiency.

In conclusion, controlling injection characteristics of the injector in compression ignition (CI) engines could lead to more efficient mixing between the injected fuel and spray propagation. Thus, additional advantages can be gained to achieve an efficient diesel engine performance, especially when using promising alternative fuels like butanol blended with diesel.

Author Contributions: S.J.M.A., A.P.W. and T.Y. conceived and designed the experiments; S.J.M.A. performed the experiments; S.J.M.A. and A.P.W. analyzed the data. S.J.M.A. wrote the paper; and A.P.W. and T.Y. provided major editorial contribution and guidance.

Acknowledgments: The first author thanks the Iraqi Government Ministry of Higher Education and Scientific Research for supporting the research. The authors are also grateful to Rishabh Choudhury for his assistance with the spray experiments and Daniel McIntyre from Diesel Care Australia Pty Ltd., Toowoomba branch, for his discussion and advice related to the common rail injection system.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Algayyim, S.J.M.; Wandel, A.P.; Yusaf, T.; Hamawand, I. The impact of n-butanol and iso-butanol as components of butanol-acetone (BA) mixture-diesel blend on spray, combustion characteristics, engine performance and emission in direct injection diesel engine. *Energy* **2017**, *140 Pt 1*, 1074–1086. [CrossRef]
2. Algayyim, S.J.M.; Wandel, A.P.; Yusaf, T.; Hamawand, I. Production and application of ABE as a biofuel. *Renew. Sustain. Energy Rev.* **2018**, *82 Pt 1*, 1195–1214. [CrossRef]
3. Algayyim, S.J.M.; Wandel, A.P.; Yusaf, T.; Al-Lwayzy, S.; Hamawand, I. Impact of butanol-acetone mixture as a fuel additive on diesel engine performance and emissions. *Fuel* **2018**, *227*, 118–126. [CrossRef]
4. Algayyim, S.J.M.; Wandel, A.P.; Yusaf, T.; Hamawand, I.; AL-Lwayzy, S. The Experimental Investigation of Butanol-Diesel Blend on Engine Performance and Emission Levels in DI Diesel Engine. In Proceedings of the 1st MoHESR and HCED Iraq Scholars Conference in Australasia 2017 (ISCA 2017), Melbourne, Australia, 5–6 December 2017; Swinburne University: Melbourne, Australia, 2017.
5. Algayyim, S.J.M.; Wandel, A.P.; Yusaf, T. The effect of Butanol-Acetone Mixture-Cottonseed Biodiesel Blend on Spray Characteristics, Engine Performance and Emissions in Diesel Engine. In Proceedings of the 11th Asia-Pacific Conference on Combustion, Sydney, Australia, 10–14 December 2017; The University of Sydney: Sydney, Australia, 2017.
6. Zaharin, M.S.M.; Abdullah, N.R.; Najafi, G.; Sharudin, H.; Yusaf, T. Effects of physicochemical properties of biodiesel fuel blends with alcohol on diesel engine performance and exhaust emissions: A review. *Renew. Sustain. Energy Rev.* **2017**, *79*, 475–493. [CrossRef]
7. Emiroğlu, A.O.; Şen, M. Combustion, performance and emission characteristics of various alcohol blends in a single cylinder diesel engine. *Fuel* **2018**, *212*, 34–40. [CrossRef]
8. Algayyim, S.J.M.; Wandel, A.P.; Yusaf, T. Experimental and Numerical Investigation of Spray Characteristics of Butanol-Diesel blends. In Proceedings of the 11th Asia-Pacific Conference on Combustion, Sydney, Australia, 10–14 December 2017; The University of Sydney: Sydney, Australia, 2017.
9. Shuai, C.; Shen, L.; Jiao, L.; Wu, Y.; Tan, Y. Identifying key impact factors on carbon emission: Evidences from panel and time-series data of 125 countries from 1990 to 2011. *Appl. Energy* **2017**, *187*, 310–325. [CrossRef]
10. Algayyim, S.J.M.; Wandel, A.; Yusaf, T.; Hamawand, I.; Al-Lwayzy, S. Experimental Study of Spray Characteristics, Engine Performance and Emission Levels of Acetone-Butanol-Ethanol Mixture-Diesel Blends in a Diesel Engine. In Proceedings of the 11th Asia-Pacific Conference on Combustion, Sydney, Australia, 10–14 December 2017; The University of Sydney: Sydney, Australia, 2017.
11. Lee, S.; Lee, C.S.; Park, S.; Gupta, J.G.; Maurya, R.K.; Agarwal, A.K. Spray characteristics, engine performance and emissions analysis for Karanja biodiesel and its blends. *Energy* **2017**, *119*, 138–151. [CrossRef]
12. Dong, P.; Yamauchi, J.; Nishida, K.; Ogata, Y. *Hole Geometrical Effect on Internal Flow, Fuel Atomization and Spray Evaporation of Multi-Hole Nozzle for Diesel Engine*; SAE Technical Paper; SAE International: Warrendale, PA, USA, 2017.
13. Suh, H.K.; Lee, C.S. A review on atomization and exhaust emissions of a biodiesel-fueled compression ignition engine. *Renew. Sustain. Energy Rev.* **2016**, *58*, 1601–1620. [CrossRef]
14. Soid, S.N.; Zainal, Z.A. Spray and combustion characterization for internal combustion engines using optical measuring techniques, A review. *Energy* **2011**, *36*, 724–741. [CrossRef]
15. Merola, S.S.; Marchitto, L.; Corcione, F.; Valentino, G.; Tornatore, C. Optical diagnostics of the pollutant formation in a CI engine operating with diesel fuel blends. *SAE Int. J. Engines* **2011**, *4*, 2543–2558. [CrossRef]
16. Huo, M.; Lin, S.; Liu, H.; Lee, C.-F.F. Study on the spray and combustion characteristics of water–emulsified diesel. *Fuel* **2014**, *123*, 218–229. [CrossRef]
17. Sazhin, S.S.; Feng, G.; Heikal, M.R. A model for fuel spray penetration. *Fuel* **2001**, *80*, 2171–2180. [CrossRef]
18. Wang, Z.; Wu, S.; Huang, Y.; Chen, Y.; Shi, S.; Cheng, X.; Huang, R. Evaporation and Ignition Characteristics of Water Emulsified Diesel under Conventional and Low Temperature Combustion Conditions. *Energies* **2017**, *10*, 1109. [CrossRef]
19. Zhang, X.; Li, T.; Ma, P.; Wang, B. Spray Combustion Characteristics and Soot Emission Reduction of Hydrous Ethanol Diesel Emulsion Fuel Using Color-Ratio Pyrometry. *Energies* **2017**, *10*, 2062. [CrossRef]
20. Verma, I.; Bish, E.; Kuntz, M.; Meeks, E.; Puduppakkam, K.; Naik, C.; Liang, L. *CFD Modeling of Spark Ignited Gasoline Engines—Part 2: Modeling the Engine in Direct Injection Mode along with Spray Validation*; No. 2016-01-0579; SAE Technical Paper: Warrendale, PA, USA, 2016.

21. Gupta, J.G.; Agarwal, A.K. *Macroscopic and Microscopic Spray Characteristics of Diesel and Karanja Biodiesel Blends*; No. 2016-01-0869; SAE Technical Paper: Warrendale, PA, USA, 2016. [CrossRef]
22. Todd, D.F.; Scott, E.P. Spray measurement technology: A review. *Meas. Sci. Technol.* **2015**, *26*, 012002.
23. Linne, M. Imaging in the optically dense regions of a spray: A review of developing techniques. *Prog. Energy Combust. Sci.* **2013**, *39*, 403–440. [CrossRef]
24. Chen, P.-C.; Wang, W.-C.; Roberts, W.L.; Fang, T. Spray and atomization of diesel fuel and its alternatives from a single-hole injector using a common rail fuel injection system. *Fuel* **2013**, *103*, 850–861. [CrossRef]
25. Ge, J.C.; Yoon, S.K.; Choi, N.J. Using Canola Oil Biodiesel as an Alternative Fuel in Diesel Engines: A Review. *Appl. Sci.* **2017**, *7*, 881. [CrossRef]
26. Kandasamy, M.; Hamawand, I.; Bowtell, L.; Seneweera, S.; Chakrabarty, S.; Yusaf, T.; Shakoor, Z.; Algayyim, S.J.M.; Eberhard, F. Investigation of Ethanol Production Potential from Lignocellulosic Material without Enzymatic Hydrolysis Using the Ultrasound Technique. *Energies* **2017**, *10*, 62. [CrossRef]
27. Trindade, W.R.D.S.; Santos, R.G.D. Review on the characteristics of butanol, its production and use as fuel in internal combustion engines. *Renew. Sustain. Energy Rev.* **2017**, *69*, 642–651. [CrossRef]
28. Rajesh Kumar, B.; Saravanan, S.; Rana, D.; Nagendran, A. A comparative analysis on combustion and emissions of some next generation higher-alcohol/diesel blends in a direct-injection diesel engine. *Energy Convers. Manag.* **2016**, *119*, 246–256. [CrossRef]
29. Armas, O.; García-Contreras, R.; Ramos, Á. Pollutant emissions from New European Driving Cycle with ethanol and butanol diesel blends. *Fuel Process. Technol.* **2014**, *122*, 64–71. [CrossRef]
30. Karabektas, M.; Hosoz, M. Performance and emission characteristics of a diesel engine using isobutanol–diesel fuel blends. *Renew. Energy* **2009**, *34*, 1554–1559. [CrossRef]
31. Doğan, O. The influence of n-butanol/diesel fuel blends utilization on a small diesel engine performance and emissions. *Fuel* **2011**, *90*, 2467–2472. [CrossRef]
32. Yao, M.; Wang, H.; Zheng, Z.; Yue, Y. Experimental study of n-butanol additive and multi-injection on HD diesel engine performance and emissions. *Fuel* **2010**, *89*, 2191–2201. [CrossRef]
33. Dobre, A.; Pană, C.; Nuţu, N.; Negurescu, N.; Cernat, A.; Bondoc, I. Bio-butanol-alternative fuel for Diesel engine. *INMATEH-Agric. Eng.* **2014**, *42*, 145–152.
34. Li, Q.; Jin, W.; Huang, Z. Laminar Flame Characteristics of C1–C5 Primary Alcohol-Isooctane Blends at Elevated Temperature. *Energies* **2016**, *9*, 511. [CrossRef]
35. Liu, H.; Lee, C.; Huo, M.; Yao, M. Comparison of ethanol and butanol as additives in soybean biodiesel using a constant volume combustion chamber. *Energy Fuels* **2011**, *25*, 1837–1846. [CrossRef]
36. Wu, H.; Nithyanandan, K.; Lee, T.H.; Lee, C.-F.F.; Zhang, C. Spray and combustion characteristics of neat acetone-butanol-ethanol, n-butanol, and diesel in a constant volume chamber. *Energy Fuels* **2014**, *28*, 6380–6391. [CrossRef]
37. Rao, D.C.K.; Karmakar, S.; Som, S.K. Puffing and Micro-Explosion Behavior in Combustion of Butanol/Jet A-1 and Acetone-Butanol-Ethanol (A-B-E)/Jet A-1 Fuel Droplets. *Combust. Sci. Technol.* **2017**, *189*, 1796–1812. [CrossRef]
38. Lešnik, L.; Vajda, B.; Žunič, Z.; Škerget, L.; Kegl, B. The influence of biodiesel fuel on injection characteristics, diesel engine performance, and emission formation. *Appl. Energy* **2013**, *111*, 558–570. [CrossRef]
39. Kang, S.; Cho, W.; Bae, C.; Kim, Y. *Influence of the Injector Geometry at 250 MPa Injection in a Light-Duty Diesel Engine*; SAE International: Warrendale, PA, USA, 2017.
40. Payri, R.; Salvador, F.J.; De la Morena, J.; Pagano, V. Experimental investigation of the effect of orifices inclination angle in multihole diesel injector nozzles. Part 2—Spray characteristics. *Fuel* **2018**, *213*, 215–221. [CrossRef]
41. Moon, S.; Gao, Y.; Park, S.; Wang, J.; Kurimoto, N.; Nishijima, Y. Effect of the number and position of nozzle holes on in-and near-nozzle dynamic characteristics of diesel injection. *Fuel* **2015**, *150*, 112–122. [CrossRef]
42. Mulemane, A.; Han, J.-S.; Lu, P.-H.; Yoon, S.-J.; Lai, M.-C. *Modeling Dynamic Behavior of Diesel Fuel Injection Systems*; No. 2004-01-0536; SAE Technical Paper: Warrendale, PA, USA, 2004. [CrossRef]
43. Lai, M.-C.; Wang, T.C.T.; Xie, X.; Han, J.-S.; Henein, N.; Schwarz, E.; Bryzik, W. *Microscopic Characterization of Diesel Sprays at VCO Nozzle Exit*; No. 982542; SAE Technical Paper: Warrendale, PA, USA, 1998. [CrossRef]
44. Kuti, O.A.; Zhu, J.; Nishida, K.; Wang, X.; Huang, Z. Characterization of spray and combustion processes of biodiesel fuel injected by diesel engine common rail system. *Fuel* **2013**, *104*, 838–846. [CrossRef]
45. Delacourt, E.; Desmet, B.; Besson, B. Characterisation of very high pressure diesel sprays using digital imaging techniques. *Fuel* **2005**, *84*, 859–867. [CrossRef]

46. Yu, W.; Yang, W.; Mohan, B.; Tay, K.L.; Zhao, F. Macroscopic spray characteristics of wide distillation fuel (WDF). *Appl. Energy* **2017**, *185*, 1372–1382. [CrossRef]
47. Yu, W.; Yang, W.; Tay, K.; Mohan, B.; Zhao, F.; Zhang, Y. Macroscopic spray characteristics of kerosene and diesel based on two different piezoelectric and solenoid injectors. *Exp. Therm. Fluid Sci.* **2016**, *76*, 12–23. [CrossRef]
48. Wang, X.; Huang, Z.; Kuti, O.A.; Zhang, W.; Nishida, K. Experimental and analytical study on biodiesel and diesel spray characteristics under ultra-high injection pressure. *Int. J. Heat Fluid Flow* **2010**, *31*, 659–666. [CrossRef]
49. Heywood, J.B. *Internal Combustion Engine Fundamentals*; McGraw-Hill: New York, NY, USA, 1988.

3.2 Summary of Article II

Spray characteristics are important for CI engines due to their effect on complete combustion. Spray characteristics of butanol-diesel blends were observed in a CVV under different operating conditions. An SA3 (Photron) high-speed camera was used to capture spray images for varying injection pressure and injection duration of two different injectors. Spray penetration, spray cone angle and spray volume were measured and calculated, using the spray edge identified from spray images.

Spray penetration of all alcohol blends was slightly further than that of neat diesel. Spray penetration was increased as a result of increased injection pressure, while the spray cone angle was slightly widened because of either increased injection pressure or injector hole diameter. Thus, efficient diesel engine performance can be achieved by controlling injection characteristics, especially when using a renewable additive blended with diesel. Therefore, fuel consumption and emissions will be reduced. Therefore, BA blended with diesel could be a good alternative fuel. Investigating the BA blend in a diesel engine will result in an understanding of its effect on diesel engine performance.

Chapter 4 - Impact of BA as a Fuel Additive for Diesel Engine

4.1 Article III

Article III: **Algayyim, S. J. M.**, Wandel, A. P., Yusaf, T., Al-Lwayzy, S., and Hamawand, I., Impact of butanol-acetone mixture as a fuel additive on diesel engine performance and emissions. *Fuel*, 2018. 227: pp. 118-126.

Butanol blend as an additive has previously been extensively investigated and tested in CI engines for various blend ratios and operating conditions. These studies support the claim that butanol as an additive in a CI engine has a number of advantages compared to ethanol, such as chemical properties (CN and heating value), improved engine performance and reduced exhaust gas emissions. However, the high production cost of butanol from fermentation makes it uncompetitive economically. An intermediate production step for butanol is as a mixture (either ABE or BA). Therefore, it is cheaper to produce BA than butanol because it is not necessary to separate the butanol from other chemicals after fermentation of the biofuel.

Many researchers have investigated the fermentation process to produce a fuel mixture of ABE with a 3:6:1 ratio. However, a number of studies demonstrate the drawbacks of using ethanol as an additive for diesel engines because of unsuitable properties for diesel engines such as lower heating value, cetane number and corrosion behaviour. Therefore, BA with no ethanol is a better additive for diesel than ABE. In a study by Li et al. (2014), BA was produced via fermentation of cassava substrate with a ratio of 2.9:1 BA.

This chapter investigates the engine performance using BA with diesel for various blend ratios and engine speeds at a 19:1 compression ratio and full load. All results are compared with neat diesel as a baseline.

Fuel 227 (2018) 118–126

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Impact of butanol-acetone mixture as a fuel additive on diesel engine performance and emissions

Sattar Jabbar Murad Algayyim[a,d,*], Andrew P. Wandel[a,b], Talal Yusaf[a], Saddam Al-Lwayzy[c], Ihsan Hamawand[c]

[a] School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, QLD 4350, Australia
[b] Computational Engineering and Science Research Centre, University of Southern Queensland, Toowoomba, QLD 4350, Australia
[c] National Centre for Engineering in Agriculture (NCEA), University of Southern Queensland, Toowoomba, QLD 4350, Australia
[d] Department of Mechanical, College of Engineering, University of Al-Qadisiyah, Al-Diwaniyah, Iraq

ARTICLE INFO

Keywords:
Butanol-acetone
Diesel engine performance
Exhaust gas emissions
Acetone-butanol-ethanol
Biomass
Fermentation

ABSTRACT

Butanol-acetone (BA) mixture is considered a green energy resource because it releases fewer emissions than other fuels. BA can produce via fermentation from biomass (agricultural waste and residues) that is non-edible. The benefits of butanol have been supported by many studies as additive fuel for conventional diesel due to its exceptional fuel properties such as high burning velocity and heating value. However, the cost of butanol production is the main issue of using it as a fuel because of high recovery and production costs. It is cheaper to produce BA than butanol because it is not necessary to separate the butanol from other chemicals in the biofuel. Many researchers have investigated the fermentation process to produce a fuel mixture of acetone-butanol-ethanol (ABE) with a 3:6:1 ratio. However, a number of studies demonstrate the drawbacks of using ethanol as an additive for diesel engines because of unsuitable properties for diesel engine such as lower heating value, cetane number and corrosion behaviour so BA with no ethanol is a better additive for diesel than ABE.

This paper investigates the effect of using a butanol/acetone (BA)-diesel blend on exhaust gas emissions and engine performance. The test was performed for different blend ratios of BA to diesel (10BA90D, 20BA80D and 30BA70D) at engine speeds of 1400, 2000 2600 RPM in a single-cylinder diesel engine. This study has shown that brake power (BP) is maximum at 10% BA at all engine speed, approximately 5% higher than D100. The brake thermal efficiency (BTE) of 10% BA was comparable with D100 at all engine speeds, but was slightly increased by 6% and 8% at all engine speeds when the BA ratio was 20% and 30% respectively. CO emission levels have a significant decrease for all BA blend with a maximum 64% reduction than D100; CO_2 emission was correlated with BP; NO_x decreased at all BA blend with a maximum 10% reduction than D100; and the exhaust gas temperature decreased for all BA blend by 15.6% compared to D100. BA is shown to be a good renewable fuel additive to diesel because it can improve energy efficiency and reduce pollutant emissions.

1. Introduction

Due to population growth together with environmental concerns, there is significant demand for carbon-neutral fuels in addition to more stringent legislation governing engine pollutant emissions. This has been attracting new interest in renewable, sustainable and environmentally - friendly energy resources [1,2]. Many techniques have been applied to reduce emissions levels and improve fuel efficiency. The use of additives such as ethanol and butanol in fossil fuels has been investigated extensively and is commercially available [3]. The experimental results of these additives revealed significant reductions in Particulate Matter (PM), hydrocarbon (HC) and carbon monoxide (CO) concentrations [4,5]. Another advantage of using alcohol additives is that they can be derived from renewable biomass resources such as residual agricultural biomass and wastes [6]. These biomass sources are widely available, but it is currently a challenging process to convert them into alcohol biofuels. Among various alcohols, ethanol is the earliest one to be put into the market [7], however some safety and technical concerns remain unresolved [8].

ABE is a combination of acetone, butanol and ethanol, which is

---

Abbreviations: ABE, acetone:butanol:ethanol; IBE, isopropanol:butanol:ethanol; BA, butanol:acetone; BP, brake power; BTE, brake thermal efficiency; BSFC, Brake specific fuel consumption; CA, crank angle; CO_2, carbon dioxide; CO, carbon monoxide; C_v, specific heat for constant volume; C_p, specific heat for constant pressure; EGT, exhaust gas temperature; NO_x, nitrogen oxides; PM, particular matter; TDC, top deep centre; UHC, unburnt hydrocarbon; θ, crank angle; γ, ratio of specific heats

[*] Corresponding author at: School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, QLD 4350, Australia.
E-mail address: Sattarjabbarmurad.algayyim@usq.edu.au (S.J.M. Algayyim).

https://doi.org/10.1016/j.fuel.2018.04.091
Received 4 December 2016; Received in revised form 13 April 2018; Accepted 18 April 2018

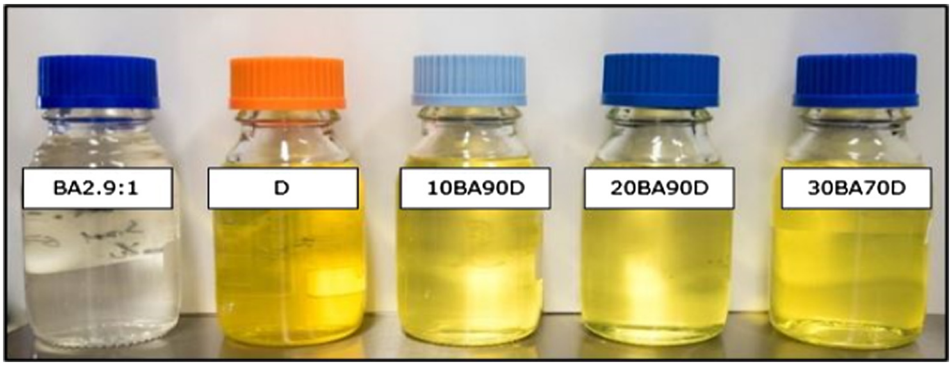


Fig. 1. Blend mixture over a period of 4 months storing.

another suitable fuel additive that can be produced from biomass via fermentation. This fuel has attracted researchers' attention due to its better performance as a blend when compared to ethanol. ABE is typically produced in a volumetric ratio of 3:6:1 from the fermentation process [9–19]. The ABE mixture can be further purified to obtain pure acetone and/or butanol. However, the purification processes significantly increase the production cost. It is preferable to use ABE as a mixture because butanol is the most abundant component in the ABE mixture. Butanol provides a higher energy content compared to ethanol and has physical properties more similar to commercial transportation fuels. Some researchers have tested the ABE mixture experimentally in CI engines. Van et al. [20] showed that ABE's laminar flame speed is higher than acetone and lower than ethanol and butanol. Other researchers [21–32] have studied the impact of ABE on various formulations of ABE (A:B:E 6:3:1, 3:6:1 and B) and ABE-diesel blends (D100, ABE20D80, ABE50D50 and ABE80D20) on spray and combustion behaviour in a constant-volume chamber. The results indicated that: ABE decreases the ignition delay and combustion temperature; soot and NO_x were remarkably reduced. The heat release rate curve of ABE20 (6:3:1) was very similar to that of D100 in terms of the ignition delay and initial premixed combustion, while the heat release rate curve of ABE20 (3:6:1) was closer to that of butanol.

Lin et al. [27] have experimentally investigated the effect of ABE-diesel blends on common-rail diesel engine performance. The results showed that addition of ABE to diesel increased the thermal efficiency and significantly reduced NO_x and soot emissions with up to 20% vol. of ABE addition to the blend. Zhao et al. [28] studied experimentally and numerically the soot mechanism of ABE with various oxygen concentrations. A multi-step ABE phenomenological soot model was proposed and implemented in the KIVA-3V Release 2 code. The results indicated reduction of soot particles under highly-diluted oxygen conditions.

Ma et al. [29] performed a droplet evaporation test of an ABE and diesel mixture in a non-combusting droplet chamber at high ambient temperatures. It was observed that the addition of the ABE mixture enhanced the evaporation speed of the droplet and thus reduced the lifespan of the droplet. Li et al. [30] studied also isopropanol-n-butanol-ethanol (IBE) as additive for gasoline with different blends ratio. It was found that IBE30 reduced CO and NO_x by (4%) and (3.3–18.6%) respectively, compared to gasoline. A number of studies [33,34] demonstrated some drawbacks when using ethanol as an additive for diesel engines because of the lower heating value and cetane number, and its corrosive behaviour. As ethanol is one of the components in ABE, another alcohol mixture, butanol-acetone (BA), has emerged. BA has a higher fraction of butanol (75%) than ABE and it does not contain ethanol. In a study by Li et al. [35], BA was produced via fermentation of cassava substrate with a ratio of 2.9:1 BA.

To our knowledge, BA as an additive to diesel fuel has not yet been investigated. In this article, a BA-diesel fuel blend was investigated in a single-cylinder diesel engine. Both the performance of the engine and exhaust emissions were tested evaluated and compared with diesel fuel.

2. Methodology

2.1. Fuel preparation and properties

Butanol-acetone was prepared with a ratio 2.9:1 using 99.8% analytical grade chemicals. The butanol used was *n*-butanol and diesel from a local petrol station. The BA (290 ml of butanol + 100 ml of acetone mixed together) which was used to simulate the intermediate product of the BA fermentation was mixed using splash blending and was blended at 4000 rpm to emulate the composition of the above-mentioned BA fermentation product.

The BA blend was blended with diesel in three ratios 10%, 20% and 30% by volume: 10BA90D, 20BA80D, and 30BA70D. Miscibility and stability of BA-diesel blends was monitored before the tests run on the engine. The visualization result of blend stability observed that there was no separation in the BA-diesel blends. Moreover, the stability of blends for phase separation was observed over a period of 4 months by storing the blends in a glass bottle (Fig. 1) the samples were visually observed every 30 days. It was observed that 10, 20 and 30% of BA blends maintained a good homogeneous mixture over a 4-month timeframe.

The density was measured for all fuel blends at 20 °C room temperature. The viscosity (kinematic viscosity at 40 °C) of the blend was measured using a Brookfield Viscometer DV-II + Pro Extra. The heating values of the blends were measured using a Digital Oxygen Bomb Calorimeter (XRY-1A). Each test was carried out in triplicate. Tables 1 and 2 illustrate the blend properties of all samples.

2.2. Engine test setup

The experiment was conducted using a G.U.N.T Hamburg single-cylinder direct injection (DI) diesel engine, designed for experimental

Table 1
Diesel fuel, *n*-butanol and acetone specifications [27,30,36].

Fuel properties	Diesel[a] fuel (C4-C12)	*n*-butanol[b] ($C_4H_{10}OH$)	Acetone[b] (C_3H_5OH)
Density @ (20 °C) (g/mL)	0.82–0.86	0.813	0.791
Viscosity@(40 °C) (mm^2/s)	1.3–2.4	2.63	0.35
Lower heating value (MJ/kg)	42.7	33.1	29.6
Auto ignition temp (°C)	230	343	465
Boiling point (°C)	180–360	118	56
Cetane number	50	≅25	

Notes:
[a] Properties of diesel are from [22].
[b] Properties of butanol and acetone are from [25,29].

Table 2
Measured properties of test blends.

Blend	Density (g/mL)@ 20 °C	Viscosity (mm^2/s)@ 40 °C	Heating value (MJ/kg)
BA	0.795	1.03	31.43
10BA90D	0.835	2	41.4
20BA80D	0.823	1.8	39.1
30BA70D	0.821	1.77	36.39

research work (Figs. 2 and 3).

Table 3 summarizes the specifications of the engine used in this study. The engine was connected to an electrical dynamometer, which was used to measure engine brake, torque and power output at various speeds. The brake power, brake thermal efficiency, brake specific fuel consumption and exhaust gas temperature were also measured. The exhaust gas emission was analysed using the Coda gas analyser to measure carbon dioxide, carbon monoxide, unburnt hydrocarbons and nitrogen oxides. The accuracy ranges of the instrumentation are listed in Table 4. A Quartz pressure sensor (CT 400.17), (measuring range up to 250 bar) with cable and measuring amplifier connected to a data acquisition system were used to record in-cylinder pressure values at 1 crank angle resolution for 12 cycles each test. The measuring amplifier processes the voltage signals coming from the sensor and sends them to the PC.

A Thermocouple transducer inserted on the exhaust system was used to measure exhaust gas temperature (EGT). The engine was heated up until steady-state conditions were reached. The engine tests were conducted at engine speeds of 1400, 2000 and 2600 RPM. Engine compression ratio kept in the ratio 19:1 of all test. Three blends 10BA90D, 20BA80D, and 30BA70D were tested along with neat diesel as a baseline for comparison with BA. Once the new fuel was pumped in, the engine was made to run for another 20 min to allow for stable operation of the new blend at test conditions. The tests of each fuel were performed 3 times; and the datasets for each fuel were then averaged to assess the experimental error.

2.3. Theoretical consideration

The heat release rate was calculated from the cylinder pressure data and crank angle readings that were recorded in the data acquisition of each test. The analysis was derived from the first law of thermodynamics for a closed system with an ideal gas after the compression stroke before the exhaust valve opens [37].

$$\frac{d\theta_n}{d\theta} = \frac{\gamma}{\gamma-1}P\frac{dV}{d\theta} + \frac{1}{\gamma-1}V\frac{dP}{d\theta}$$
$$= \left(\frac{\gamma}{\gamma-1} \times P_I \times (V_{i+1}-V_i) + \frac{1}{\gamma-1} \times V_I \times (P_{i+1}-P_i)\right) \Big/ \Delta\theta$$

Here: $dQ_n/d\theta$ is the heat release rate per crank angle (CAD), $\gamma = c_p/c_v = 1.35$ is the ratio of specific heats. The input values are the pressure data (collected as function of crank angle) and the cylinder volume V at any crank angle θ (calculated from the engine geometry).

3. Results and discussion

3.1. In-cylinder pressure and heat release rate

A recording is made of the indicator (in-pressure cylinder) data for 12 cycles in a contiguous file, with a sampling rate corresponding to each 1 degree of crank angle. The evolution of in-cylinder pressure with CAD was an average of three runs. Figs. 4–6 show the indicated pressure at 1400, 2000 and 2600 RPM for the entire test blends. It can be seen, there was a difference in the pressure curves due to different BA ratio in the blends. The pressure rise in Fig. 4 shows that 10BA is highest for 1400 rpm so maximum pressure monotonically decreases with BA at this speed and compared to diesel, but 20BA has the highest pressure for the other speeds. In addition, the biggest ignition delay was at 20%BA than other BA ratio and compared to diesel at all speeds. With low engine speed there were no fluctuations in the in-cylinder pressure trend due to more stable combustion. However, with high alcohol ratios (20% and 30%) in diesel, the combustion was less stable at fast engine speeds, there less time for combustion.

A relatively higher-pressure rise is important to improve engine thermal efficiency. This improves combustion due to ignition delay that allows more mixing time of air with fuel, higher speed flame and lower equivalence ratio at the flame front due to the high oxygen content of the BA. Fig. 7 shows the standard deviation of the maximum pressure observed in each test. It can be realized that BA blends have a less pressure deviation from the average value than diesel. BA10D90 blend showed less stable combustion by indicating a higher standard deviation at 2600 speeds than the other blends. 20% BA showed a higher standard deviation at 2000 speeds.

Figs. 8–10) present the local maxima of heat release rate. As a possible explanation of the behavior of the BA fuels, the following mechanism can be considered: the cetane number of the blends decreases with the addition of BA (due to the high ratio of butanol 75% in BA); and the boiling point of BA is lower. From the graphs, it is noticeable that increasing the BA content caused an increase in heat release rate after TDC.

Therefore, the combustible amount increased during ignition delay and combustion period, and consequently further resulted in maximum heat release rate when testing the oxygenate additive fuel blends in CI engines [38]. The maximum heat release rate at 1400 rpm and 2000 rpm was for 30BA-diesel (Figs. 8 and 9) because 30BA causes the reaction time to be longer and closer to TDC. However, the lowest maximum heat release rate observed at 2600 rpm was 30BA-diesel; the high levels of noise at this speed make it difficult to draw firm

Fig. 2. Engine and control board.

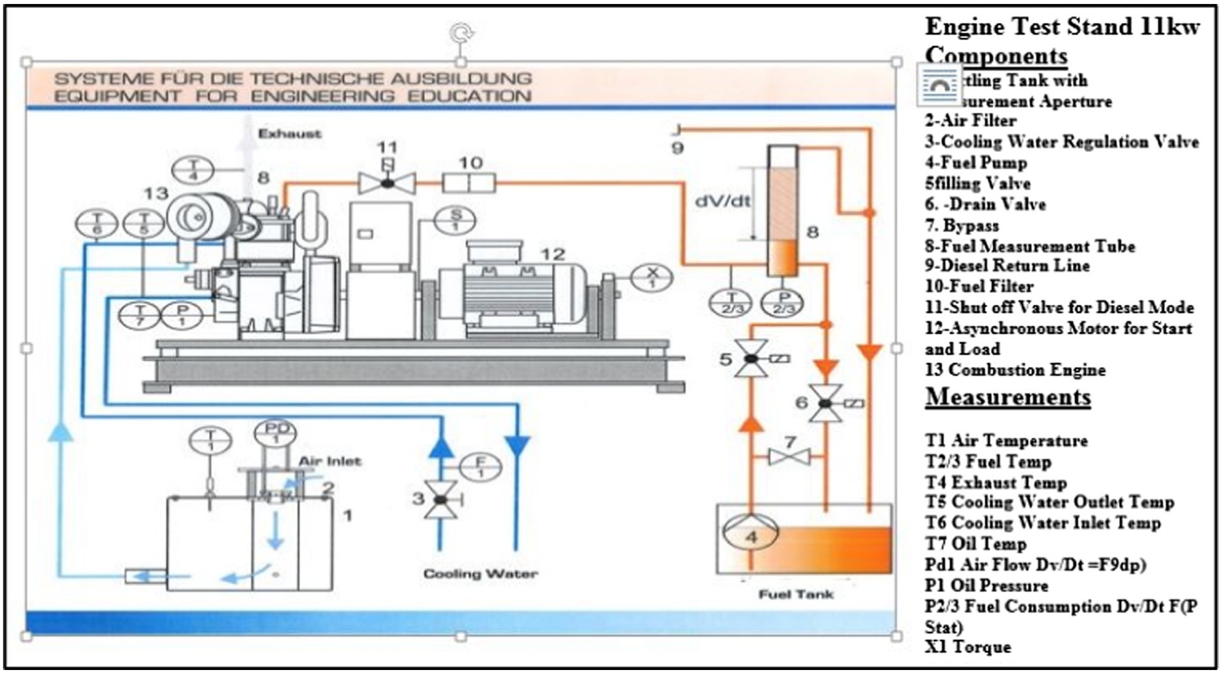


Fig. 3. Engine components and measurements.

Table 3
Engine specifications.

Engine Manufacturer	Farymann
Engine model	G.U.N.T. Hamburg
Combustion type	Direct Injection Engine, with 3-hole nozzle
Number of cylinders	1
Compression ratio	5:1–19:1
Maximum compression pressure	60–80 bar
Maximum power (kW)	Approx. 6 kW
Speed range (RPM)	900–3000
Bore	90 mm
Stroke	74 mm
Capacity	470 cm^3
Crank radius	37 mm
Connecting rod length	128 mm
Nozzle injection pressure	300 bar
Engine speed (rpm)	1400, 2000 and 2600
Compression ratio	19:1
Test blends	D, 10BA, 20BA and 30BA

Table 4
Instrumentation.

Parameter	Source	Resolution	Accuracy
Torque	Load cell on dynamometer	0.001 nm	1%
Speed	Tachometer on output shaft	0.0001 rpm	0.03%
Exhaust Gas Temperature	Thermocouple in exhaust manifold	0.001 °C	1 °C
Fuel Flow	Mass flow meter	0.001 L/min	0.1%
Exhaust Gas Composition	Coda gas analyser	0.1% CO_2, 100 ppm NO_x, 10 ppm UHC, 0.01% CO	0.1% NO_x, 0.01% UHC
In-Cylinder Pressure	Pressure transducer in cylinder in cylinder head	0.01 bar	1%

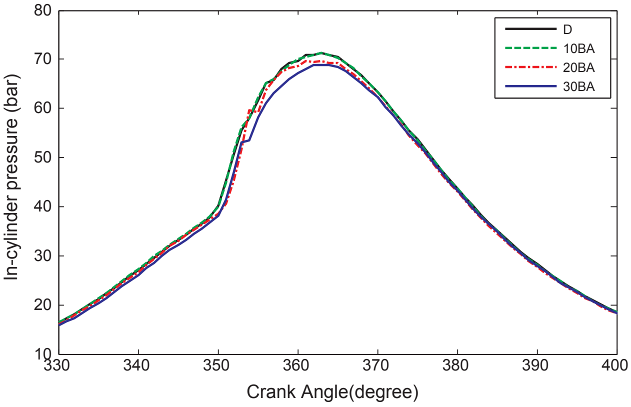


Fig. 4. Evolution of in-cylinder pressure with CAD for the blends at 1400 rpm engine speed.

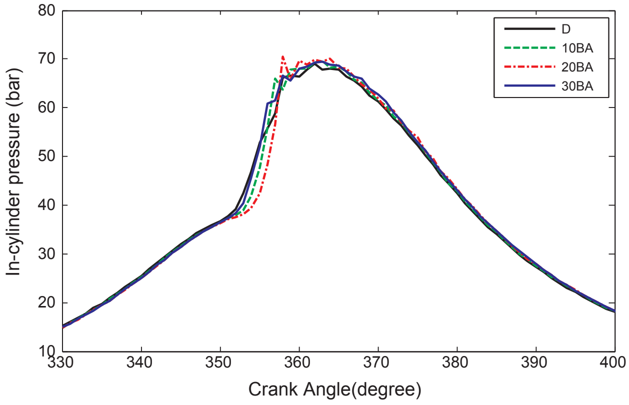


Fig. 5. Evolution of in-cylinder pressure with CAD for the blends at 2000 rpm engine speed.

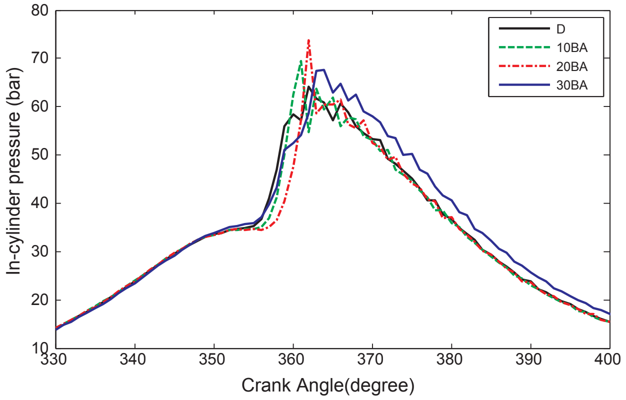


Fig. 6. Evolution of in-cylinder pressure with CAD for the blends at 2600 rpm engine speed.

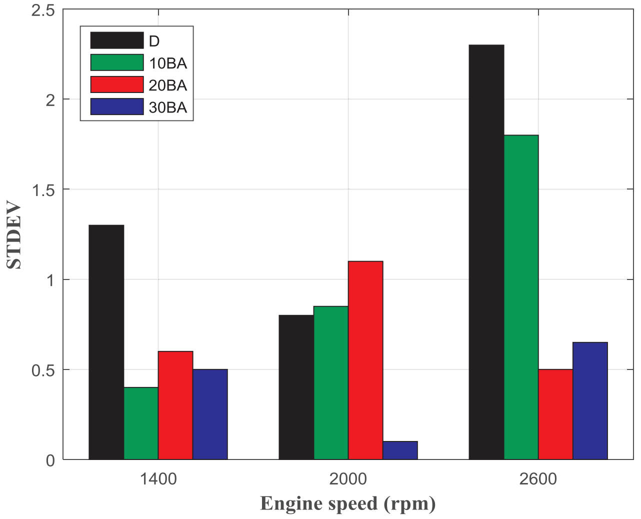


Fig. 7. Standard deviation of the maximum pressure observed. Results are shown for in each blend at three engine speeds.

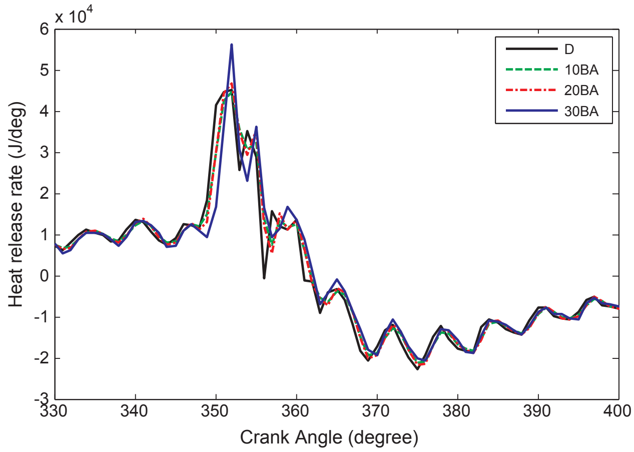


Fig. 8. Heat release rate with CAD for the blends at 1400 rpm engine speed.

conclusions. The lower viscosity and the higher heat of vaporisation of 30BA-diesel may be the causes of this behavior.

3.2. Statistical analysis

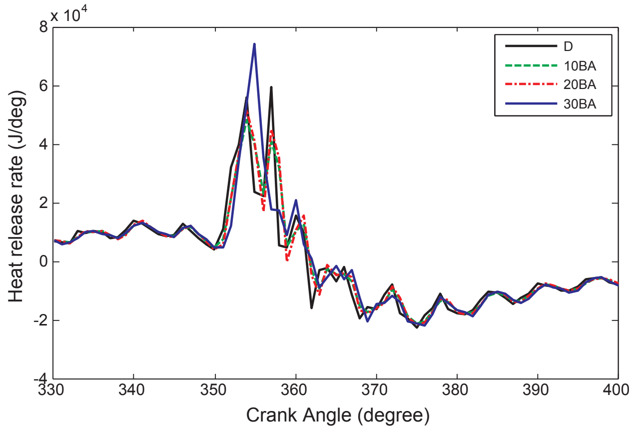


Fig. 9. Heat release rate with CAD for the blends at 2000 rpm engine speed.

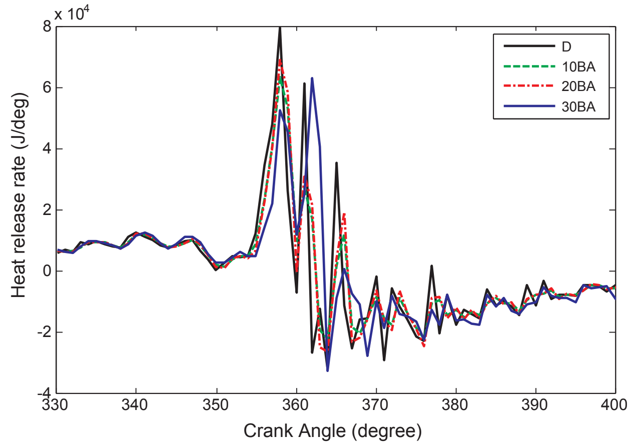


Fig. 10. Heat release rate with CAD for the blends at 2600 rpm engine speed.

Table 5
Summary of one-way ANOVA of the effect on the type of fuel on the engine performance and emission parameters.

Dependent variable	Degrees of freedom	Mean Square	F	Sig*
BP	3.0	0.019	0.019	0.996
BSFC	3.0	402.731	2.998	0.095
EGT	3.0	1141.751	0.250	0.859
NO_x	3.0	974	0.41	0.756
UHC	3.0	616.8	1.429	0.304
CO	3.0	0.372	1.243	0.356
CO_2	3.0	0.105	0.172	0.912

* Mean difference is significant if $p \leq 0.05$.

The experimental data of engine performance and exhaust gas emissions were analysed using the IBM SPSS statistics software. One-way ANOVA and Bonferroni post hoc tests were performed to study the differences between the fuel types for engine performance and emissions with a significance level of $p < 0.05$ [39] (Table 5).

3.3. Brake power (BP) and torque (T)

Figs. 11 and 12 present the relationship between engine torque and power and different engine speeds, respectively. The engine was fuelled with different ratios of BA-diesel blends of 10%, 20%, and 30% BA and the results from these tests were compared with diesel fuel. The torque was found to be slightly increased for 10BA-diesel at all engine speeds. However, the torque of 20% and 30% BA-diesel was a slight decrease in all engine speed. The brake power has slightly increased at all engine speed only in the case of the BA ratio of 10% with 5% increment compared with D100.

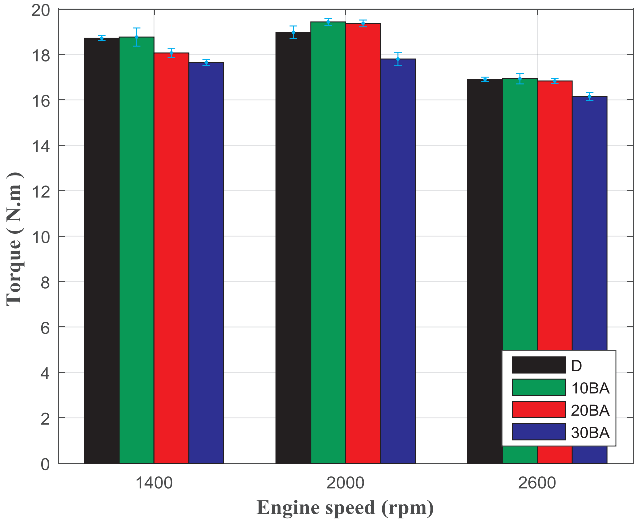


Fig. 11. Torque (N.m) at different speeds fuelled with different BA ratios and compared with diesel fuel as baseline.

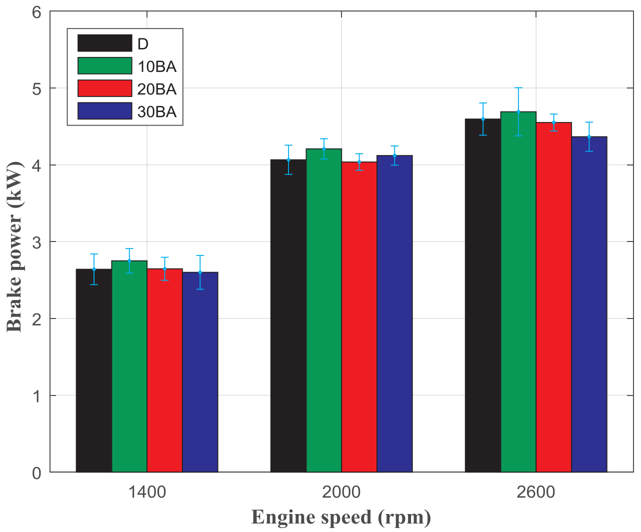


Fig. 12. Engine brake power (kW) at different speed fuelled with different BA ratios and compared with diesel fuel as baseline.

3.4. Brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE)

The effect of BA-diesel fuel blends on BSFC and BTE with the variation of engine speed are illustrated in Figs. 13 and 14, respectively. It was observed that all BA-diesel fuel blends increased the BSFC and BTE at all BA blend ratios. The BSFC of the 10BA, 20BA and 30BA diesel fuel increased by, 5.5–6.5%, 1.1–3.45% and 5–14%, respectively, compared with regular diesel at the three-engine speed. With the increased BA addition, the heating value of the BA-diesel decreased by 6.5% at 30BA ratio, which influenced on BSFC significantly. A number of current and previous research has reported similar results of the impact of higher fraction of oxygenated compounds on BSFC of diesel engines. These studies supported the claim that a higher concentration of oxygenated compounds, such as ethanol or butanol and ABE, in fuel mixture reduced the heating value and led to increase the fuel consumption [25,28,29,40]. Therefore, it needs more fuel to match the diesel fuel power.

In spite of the fact that BA-diesel fuel blend has increased the BSFC, higher BTE was achieved due to the higher oxygen content in the blend. As shown in Fig. 14 comparable BTE has been achieved with 10% BA blend ratio at all engine speeds. However, BTE was increased by 6% and 8% when the BA ratio was 20% and 30% at all engine speeds. Rakopoulos et al. [41,42] investigated the effect of butanol-diesel and reported that BTE was slightly increased than for diesel. These increments in BTE were achieved because of increased oxygen content in the blend. Oxygen helps to improve the combustion efficiency, particularly during the diffusion combustion phase. Another influential factor that affects the BTE is cetane number. BA-diesel fuel blends have a lower cetane number than diesel, which causes longer ignition delay, consequently a wider range in the fraction of fuel burned in the premixed mode, this elevates BTE. In addition, flame-burning speed of fuels is an important aspect that is related to the brake thermal efficiency. Higher laminar flame speed leads to higher brake thermal efficiency. Larger chain alcohols such as butanol has higher flame-burning speed [43,44]. Laminar burning velocities for diesel and butanol are 33 cm/s [45] and 45 cm/s [46], respectively. So, the high ratio of butanol in the BA mixture in the reason for the higher BTE.

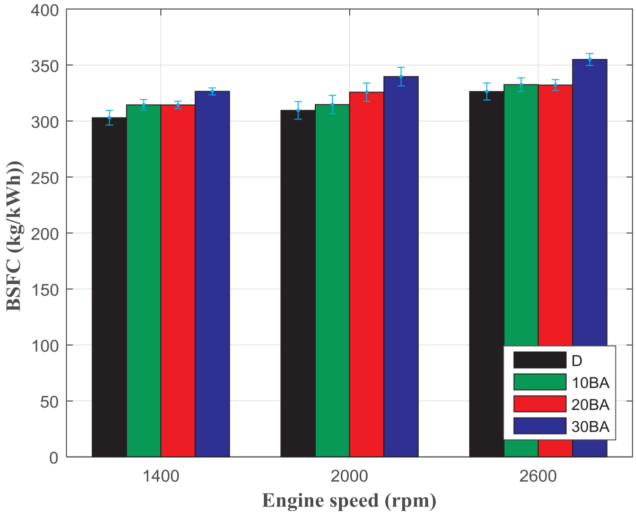


Fig. 13. BSFC (kg/kW h) at different engine speeds fuelled with different BA ratios and compared with diesel fuel as baseline.

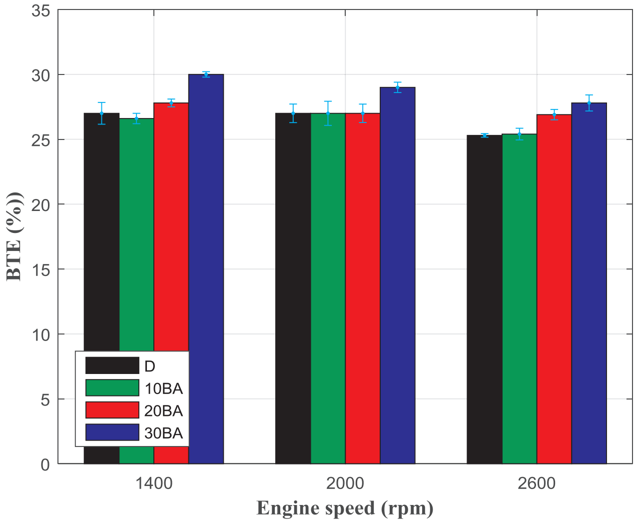


Fig. 14. BTE at different engine speeds fuelled with different BA ratio and compared with diesel fuel as baseline.

3.5. Exhaust gas temperature (EGT) and NOx formation

Fig. 15 shows the effect of BA-diesel fuel blend on exhaust gas

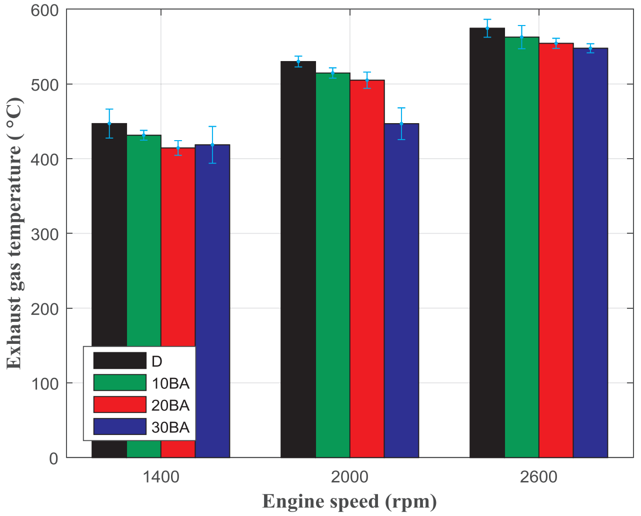


Fig. 15. The relation between exhaust gas temperatures (EGT) with different engine speed fuelled with different BA ratios.

temperature at various engine speeds. It was observed that exhaust gas temperature of 10BA, 20BA and 30BA-diesel fuel blends reduced by, 2.1–3.5%, 3.4–7.3% and 4.6–15.6%, respectively, compared with regular diesel at the three engine speeds. This reduction may be due to the lower energy content and higher oxygen of the BA-diesel fuel blends. The increasing molecular oxygen content of the fuel blends affects combustion temperature and decreases the energy content of the fuel. Furthermore, Ref. [41] reported that the latent heat of vaporisation of *n*-butanol (585 kJ/kg) (the ratio of butanol in BA is about 75%) is higher than diesel (250 kJ/kg), so BA-diesel fuel has a higher latent heat of evaporation. Because of these factors, BA-diesel blend showed a significant effect on the exhaust gas temperature. Similar trend results were observed in studies of butanol-diesel blend [41,47].

The effect of BA-diesel fuel blends on NO_x emission with the variation of engine speed is illustrated in Fig. 16. NO_x emission of 10BA, 20BA and 30BA-diesel fuel blends reduced by 2.2–10%, 2.2–7.5% and 2.64–6.6%, respectively, compared with regular diesel at the three engine speeds due to decreased exhaust gas temperature as mentioned above (Fig. 15). Similar trend results were observed in studies of butanol-diesel blend [41,47].

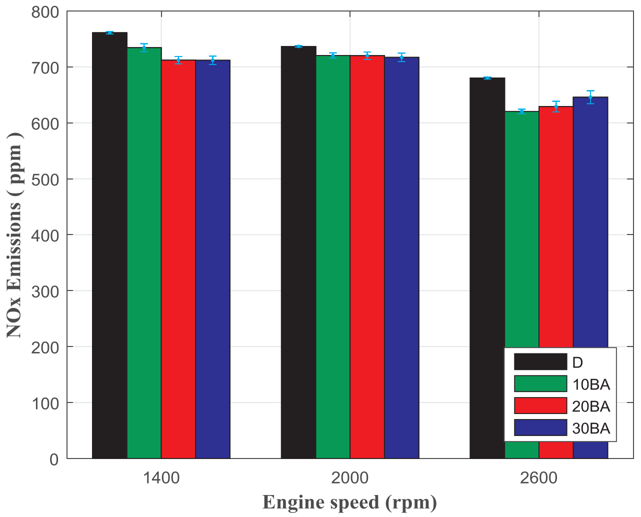


Fig. 16. The relation between NO_x emissions with different engine speed fuelled with different BA ratios.

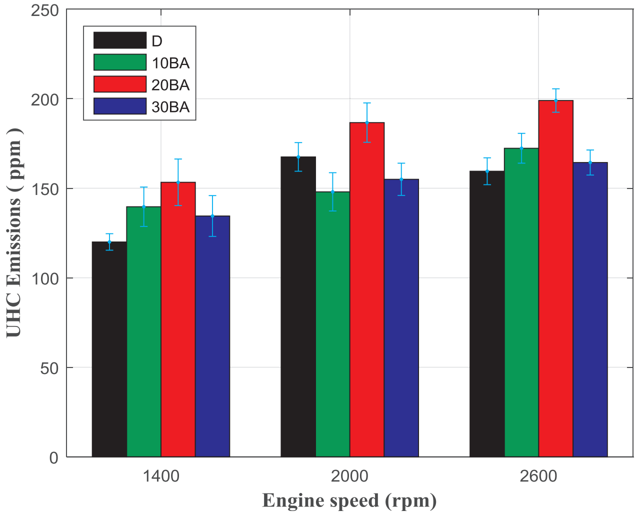


Fig. 17. The relation between UHC emissions and engine speed for different blend ratios of BA.

3.6. Unburnt hydrocarbon (UHC)

The unburnt hydrocarbon content (UHC) of the exhaust gas emission with different engine speed for different blend ratio of BA is presented in Fig. 17. UHC emission of 10BA, 20BA and 30BA-diesel fuel blends increased by 8–16.3%, 11.4–37.3% and 3–12%, respectively, compared with regular diesel at the 1400 and 2600 rpm at all BA blend ratios. Generally, BA-diesel fuel blends emitted higher UHC emissions than diesel fuel. This is mainly due to the combined effects of the lower cetane number and higher heat of vaporisation of the blends. A lower cetane number of the BA-diesel fuel blends delays the ignition and allows more time for fuel blends to evaporate. Moreover, the higher heat of vaporisation of BA-diesel fuel blends leads to slower evaporation. Therefore, there is an insufficient time to complete the reaction. Similar trend results were observed in Refs.[41,47–49].

3.7. Carbon monoxide (CO) and carbon dioxide (CO_2)

CO emissions can be formed via a number of mechanisms. A rich mixture will lead to increase CO emission. Fig. 18 shows CO emission level for the different ratio of BA at different engine speeds. The figure shows a noticeable decrease in CO emission level of 10, 20 and 30BA-

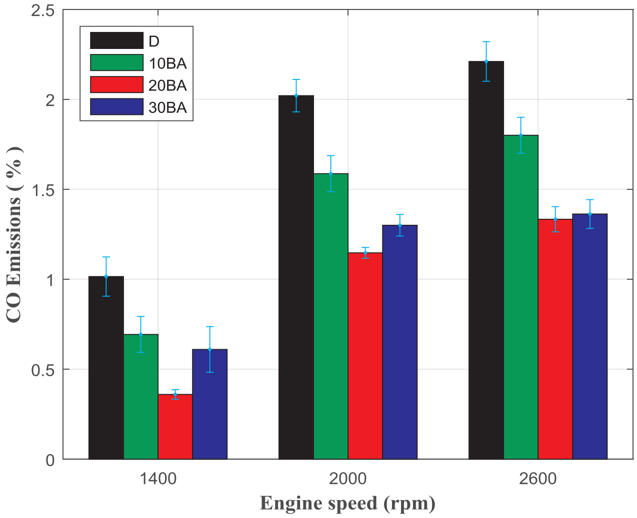


Fig. 18. The relation between CO and engine speeds tested by using different blend ratio of BA.

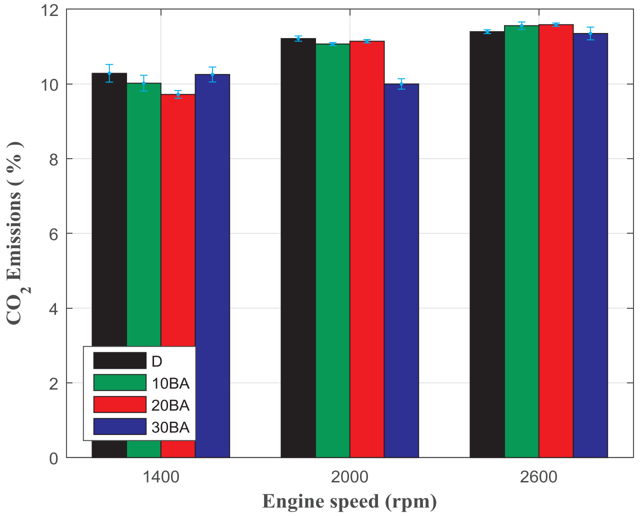


Fig. 19. The relation between CO_2 and engine speeds tested by using different blend ratio of BA and compared with diesel fuel as baseline.

diesel by 18.5–41%, 39.8–64.5% and 35.6–39.9%, respectively, compared with regular diesel due to complete combustion consequences of high oxygen content of BA. The higher oxygen content of BA-diesel fuel blends can promote the oxidation of CO and enhance the complete combustion, resulting in lower CO emissions. Similar results were observed in Refs. [41,47].

Fig. 19 presents the relation of CO_2 emission levels at different engine speeds and BA blend ratios. The figure shows that CO_2 emission was correlated with brake power (BP) at almost all engine speeds and BA ratios.

4. Conclusions

This experimental study revealed the potential of BA-diesel blends as a promising renewable fuel for CI engine that can be produced by fermentation of waste lignocellulosic material process. The engine performance and emission characteristics between BA-diesel blend and diesel fuels were compared. Some conclusions are as follows: It was found that the combustion phasing was advanced with increasing BA content, which can improve the combustion quality because of the high oxygen content and reduced combustion duration. As a result, 10% BA showed 5% improvement in BP relative to D100, while 20% and 30% BA showed a comparable BP, at all engine speeds. BTE of 10% BA blend was comparable to D100 at all engine speeds; and 6% and 8% higher BTE for BA 20 and 30 at all engine speeds. For the emissions, BA-diesel blend provided better result based on its maximum lower CO (64.5%), NO_x (10%) emissions and exhaust gas temperature (15.6%) than those of D100, although UHC was increased by 37.3%.

BA could be a promising alternative additive for diesel fuel because it can be fermented from non-edible biomass feedstock and without requiring a recovery process to obtain a pure chemical. BA also has the potential for improving diesel engine performance and decreasing exhaust emissions.

Acknowledgments

The first author would like to thank the Iraqi Government Ministry of Higher Education and Scientific Research for supporting the research. The authors are also grateful to Dr Paul Baker for helpful discussions and Mr Robert Kimber for his assistance with the engine experiments.

References

[1] Algayyim SJM, Wandel AP, Yusaf T, Hamawand I. Production and application of ABE as a biofuel. Renew Sustain Energy Rev 2018;82(Part 1):1195–214.
[2] Algayyim SJM, Wandel AP, Yusaf T, Hamawand I, Al-Lwayzy S. Experimental study of spray characteristics, engine performance and emission levels of acetone-butanol-ethanol mixture-diesel blends in a diesel engine. 11th Asia-Pacific Conference on Combustion. NSW Australia: The University of Sydney; 2017. 10th–14th December.
[3] Algayyim SJM, Wandel AP, Yusaf T. Experimental and numerical investigation of spray characteristics of butanol-diesel blends. 11th Asia-Pacific Conference on Combustion. NSW Australia: The University of Sydney; 2017. 10th–14th December.
[4] Atmanli A, Ileri E, Yuksel B, Yilmaz N. Extensive analyses of diesel–vegetable oil–n-butanol ternary blends in a diesel engine. Appl Energy 2015;145:155–62.
[5] İleri E. Experimental investigation of the effect of diesel–cotton oil–n-butanol ternary blends on phase stability, engine performance and exhaust emission parameters in a diesel engine. Fuel 2013;109:503–11.
[6] Kandasamy M, Hamawand I, Bowtell L, Seneweera S, Chakrabarty S, Yusaf T, et al. Investigation of ethanol production potential from lignocellulosic material without enzymatic hydrolysis using the ultrasound technique. Energies 2017;10(1):62.
[7] Herzog C, Fryszman A. Perspectives for the utilization of renewable fuels in Latin America. SAE Technical Paper; 1991.
[8] Giakoumis EG, Rakopoulos DC, Rakopoulos CD. Combustion noise radiation during dynamic diesel engine operation including effects of various biofuel blends: a review. Renew Sustain Energy Rev 2016;54:1099–113.
[9] Nasib Q, Sahaa BC, Hectora RE, Hughes SR, Cottaa MA. Butanol production from wheat straw by simultaneous saccharification and fermentation using Clostridium beijerinckii: Part I—Batch fermentation. Biomass Bioenergy 2008;32:168–75.
[10] Green EM. Fermentative production of butanol—the industrial perspective. Curr Opin Biotechnol 2011;22(3):337–43.
[11] Kujawska A, Kujawski J, Bryjak M, Kujawski W. ABE fermentation products recovery methods—a review. Renew Sustain Energy Rev 2015;48:648–61.
[12] Bellido C, Infante C, Coca M, González-Benito G, Lucas S, García-Cubero MT. Efficient acetone–butanol–ethanol production by *Clostridium beijerinckii* from sugar beet pulp. Bioresour Technol 2015;190:332–8.
[13] Qureshi N, Blaschek H. ABE production from corn: a recent economic evaluation. J Ind Microbiol Biotechnol 2001;27(5):292–7.
[14] Moradi F, Amiri H, Soleimanian-Zad S, Ehsani MR, Karimi K. Improvement of acetone, butanol and ethanol production from rice straw by acid and alkaline pretreatments. Fuel 2013;112:8–13.
[15] Zhang Y, Hou T, Li B, Liu C, Mu X, Wang H. Acetone-butanol-ethanol production from corn stover pretreated by alkaline twin-screw extrusion pretreatment. Bioprocess Biosyst Technol 2014;37(5):913–21.
[16] Ni Y, Sun Z. Recent progress on industrial fermentative production of acetone-butanol-ethanol by *Clostridium acetobutylicum* in China. Appl Microbiol Biotechnol 2009;83(3):415–23.
[17] Abd-Alla MH, Zohri AN, El-Enany AW, Ali SM. Acetone-butanol-ethanol production from substandard and surplus dates by Egyptian native Clostridium strains. Anaerobe 2015;32:77–86.
[18] Yang M, Zhang J, Kuittinen S, Vepsäläinen J, Soininen P, Keinänen M, et al. Enhanced sugar production from pretreated barley straw by additive xylanase and surfactants in enzymatic hydrolysis for acetone–butanol–ethanol fermentation. Bioresour Technol 2015;189:131–7.
[19] Sunwoo IY, Hau NT, Ra CH, Jeong G-T, Kim S-K. Acetone-Butanol-Ethanol production from waste seaweed collected from Gwangalli Beach, Busan, Korea, based on pH-controlled and sequential fermentation using two strains. Appl Biochem Biotechnol 2018.
[20] Van Geem KM, Cuoci A, Frassoldati A, Pyl SP, Marin GB, Ranzi E. An experimental and kinetic modeling study of pyrolysis and combustion of acetone–butanol–ethanol (ABE) mixtures. Combust Sci Technol 2012;184(7–8):942–55.
[21] Wu H, Nithyanandan K, Zhang J, Lin Y, Lee TH, Lee C, et al. Impacts of acetone–butanol–ethanol (ABE) ratio on spray and combustion characteristics of ABE–diesel blends. Appl Energy 2015;149:367–78.
[22] Wu H, Nithyanandan K, Zhou N, Lee TH, Lee C-FF, Zhang C. Impacts of acetone on the spray combustion of Acetone–Butanol–Ethanol (ABE)-Diesel blends under low ambient temperature. Fuel 2015;142:109–16.
[23] Wu H, Nithyanandan K, Lee TH, Lee C-FF, Zhang C. Spray and combustion characteristics of neat acetone-butanol-ethanol, n-butanol, and diesel in a constant volume chamber. Energy Fuels 2014;28(10):6380–91.
[24] Zhou N, Huo M, Wu H, Nithyanandan K, Lee C-FF, Wang Q. Low temperature spray combustion of acetone–butanol–ethanol (ABE) and diesel blends. Appl Energy 2014;117:104–15.
[25] Lin Y, Wu H, Nithyanandan K, Lee TH, Chia-fon FL, Zhang C. Investigation of high percentage acetone-butanol-ethanol (ABE) blended with diesel in a constant volume chamber. ASME 2014 Internal Combustion Engine Division Fall Technical Conference. American Society of Mechanical Engineers; 2014.
[26] Lee TH, Lin Y, Wu H, Meng L, Hansen A, Lee C-F. Characterization spray and combustion processes of acetone-butanol-ethanol (ABE) in a constant volume chamber. SAE Technical Paper; 2015.
[27] Lin Y, Lee T, Nithyanandan K, Zhang J, Li Y, Lee C-F. Experimental investigation and analysis of combustion process in a diesel engine fueled with acetone-butanol-ethanol/diesel blends. SAE International; 2016.
[28] Zhao Z, Xu Z, Liu J, Wang M, Lee C-F, Chang W, Hou J. Experimental and numerical investigation of soot mechanism of acetone-butanol-ethanol (ABE) with various oxygen concentrations. SAE Int J Engines 2015:1.
[29] Ma X, Zhang F, Han K, Yang B, Song G. Evaporation characteristics of

acetone–butanol–ethanol and diesel blends droplets at high ambient temperatures. Fuel 2015;160:43–9.

[30] Li Y, Meng L, Nithyanandan K, Lee TH, Lin Y, Lee C-FF, et al. Combustion, performance and emissions characteristics of a spark-ignition engine fueled with isopropanol-n-butanol-ethanol and gasoline blends. Fuel 2016;184:864–72.

[31] Zhang Z, Zhu S, Liang J, Tian L, Li G. Experimental and kinetic studies of premixed laminar flame of acetone-butanol-ethanol (ABE)/air. Fuel 2018;211(Suppl. C):95–101.

[32] Luo J, Zhang Y, Zhang Q, Liu J, Wang J. Evaluation of sooting tendency of acetone-butanol-ethanol (ABE) fuels blended with diesel fuel. Fuel 2017;209(Suppl. C):394–401.

[33] Park SH, Youn IM, Lee CS. Influence of ethanol blends on the combustion performance and exhaust emission characteristics of a four-cylinder diesel engine at various engine loads and injection timings. Fuel 2011;90(2):748–55.

[34] Huang J, Wang Y, Li S, Roskilly AP, Yu H, Li H. Experimental investigation on the performance and emissions of a diesel engine fuelled with ethanol–diesel blends. Appl Therm Eng 2009;29(11–12):2484–90.

[35] Li X, Li Z-G, Shi Z-P. Metabolic flux and transcriptional analysis elucidate higher butanol/acetone ratio feature in ABE extractive fermentation by *Clostridium acetobutylicum* using cassava substrate. Bioresour. Bioprocess. 2014;1(1):1–13.

[36] Chong CT, Hochgreb S. Measurements of laminar flame speeds of liquid fuels: Jet-A1, diesel, palm methyl esters and blends using particle imaging velocimetry (PIV). Proc Combust Inst 2011;33(1):979–86.

[37] Heywood JB. Internal combustion engine fundamentals. New York: McGraw-Hill; 1988.

[38] Chen H, Wang J, Shuai S, Chen W. Study of oxygenated biomass fuel blends on a diesel engine. Fuel 2008;87(15–16):3462–8.

[39] Al-lwayzy SH, Yusaf T. Diesel engine performance and exhaust gas emissions using Microalgae *Chlorella protothecoides* biodiesel. Renewable Energy 2017;101:690–701.

[40] Siwale L, Kristóf L, Adam T, Bereczky A, Mbarawa M, Penninger A, et al. Combustion and emission characteristics of n-butanol/diesel fuel blend in a turbo-charged compression ignition engine. Fuel 2013;107:409–18.

[41] Rakopoulos DC, Rakopoulos CD, Giakoumis EG, Dimaratos AM, Kyritsis DC. Effects of butanol–diesel fuel blends on the performance and emissions of a high-speed DI diesel engine. Energy Convers Manage 2010;51(10):1989–97.

[42] Rakopoulos D, Rakopoulos C, Hountalas D, Kakaras E, Giakoumis E, Papagiannakis R. Investigation of the performance and emissions of bus engine operating on butanol/diesel fuel blends. Fuel 2010;89(10):2781–90.

[43] Farrell J, Johnston R, Androulakis I. Molecular structure effects on laminar burning velocities at elevated temperature and pressure. SAE Paper 2004;1:2936–58.

[44] Wallner T, Miers SA, McConnell S. A comparison of ethanol and butanol as oxygenates using a direct-injection, spark-ignition engine. J Eng Gas Turbines Power 2009;131(3):032802.

[45] Sayin C. Engine performance and exhaust gas emissions of methanol and ethanol–diesel blends. Fuel 2010;89(11):3410–5.

[46] Sarathy SM, Thomson MJ, Togbé C, Dagaut P, Halter F, Mounaim-Rousselle C. An experimental and kinetic modeling study of n-butanol combustion. Combust Flame 2009;156(4):852–64.

[47] Rakopoulos DC, Rakopoulos CD, Hountalas DT, Kakaras EC, Giakoumis EG, Papagiannakis RG. Investigation of the performance and emissions of bus engine operating on butanol/diesel fuel blends. Fuel 2010;89(10):2781–90.

[48] Miers SA, Carlson RW, McConnell SS, Ng HK, Wallner T, LeFeber J, Video EI. Drive cycle analysis of butanol/diesel blends in a light-duty vehicle. Argonne National Laboratory (ANL); 2008.

[49] Rakopoulos DC, Rakopoulos CD, Papagiannakis RG, Kyritsis DC. Combustion heat release analysis of ethanol or n-butanol diesel fuel blends in heavy-duty DI diesel engine. Fuel 2011;90(5):1855–67.

4.2 Summary of Article III

This experimental study revealed the potential of using BA-diesel blends as a promising renewable fuel for CI engines that can be produced by fermentation of waste lignocellulosic material. BA blends can easily be blended with diesel at any ratio. All BA-diesel blends maintained a good homogeneous mixture over a long timeframe. The combustion phasing was advanced with increasing BA content, largely as a result of the high oxygen content, which can improve the combustion quality because of the potential for an extended combustion duration. There is some improvement in brake power with 10% of BA in diesel blend. High blend ratios of BA showed increments in brake thermal efficiency (BTE) for all engine speeds. Exhaust gas temperature (EGT) was reduced as a result of blended BA with neat diesel. NO_x and CO emissions of all BA-diesel blends were decreased compared to neat diesel.

Therefore, BA could be a promising alternative additive for diesel fuel because it can be fermented from non-edible biomass feedstock and without requiring a recovery process to obtain a pure chemical. BA also has the potential for improving diesel engine performance and decreasing exhaust emissions.

Butanol’s structure has carbon atoms classified in two chains (straight and branched) and has four different isomers: normal butanol (n-butanol), secondary butanol (sec-butanol), iso-butanol and tertiary butanol (tert-butanol). All butanol isomers can decrease exhaust gas emission levels because they are highly oxygenated. However, the option of using sec-butanol and tert-butanol as future biofuels is unclear because their production processes by fermentation are not yet established in the bio-butanol industry. All studies have focused on using n-butanol or iso-butanol blended separately with diesel, with various results. Therefore, researching iso-butanol and n-butanol as potential additive fuels is an emerging research area. By using iso-BA or n-BA, there is an extra reduction in cost compared to neat butanol. While there are many fermentation techniques that can control the final type of butanol isomers in BA fermentation, using a mixture of n-butanol or iso-butanol as components of the BA mixture with diesel shows promise for optimising the additive composition, and is the focus of Chapter 5.

Chapter 5 - Impact of n-B and iso-B on Spray and Engine Performance

5.1 Article IV

Article IV: **Algayyim, S. J. M.**, Wandel, A. P., Yusaf, T., and Hamawand, I., The impact of n-butanol and iso-butanol as components of butanol-acetone (BA) mixture-diesel blend on spray, combustion characteristics, engine performance and emission in direct injection diesel engine. *Energy*, 2017. 140 (Part 1): pp. 1074-10.

This chapter assesses the impact of nB and isoB as components of a butanol-acetone BA mixture blended with diesel on spray, combustion, engine performance and emission characteristics. The macroscopic spray characteristics including spray penetration, spray cone angle and spray volume were measured at two injection pressures: 300 bar and 500 bar. Direct visualisation of images from a high-speed camera was used in the analysis. Two blend ratios (10% and 20%) of iso- and n-BA-diesel blends were tested in a single-cylinder DI diesel engine at three engine speeds: 1400, 2000 and 2600 rpm at full load. All results were compared to neat diesel as a baseline.

Energy 140 (2017) 1074–1086

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

The impact of n-butanol and iso-butanol as components of butanol-acetone (BA) mixture-diesel blend on spray, combustion characteristics, engine performance and emission in direct injection diesel engine

Sattar Jabbar Murad Algayyim [a], [*], Andrew P. Wandel [b], Talal Yusaf [a], Ihsan Hamawand [a]

[a] School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, QLD, 4350, Australia
[b] Computational Engineering and Science Research Centre, School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, QLD, 4350, Australia

ARTICLE INFO

Article history:
Received 9 June 2017
Received in revised form
5 August 2017
Accepted 11 September 2017
Available online 14 September 2017

Keywords:
Butanol-acetone mixture
iso-Butanol
n-Butanol
Spray characteristics
Diesel engine performance
Emissions

ABSTRACT

This article assesses the impact of n-butanol (nB) and iso-butanol (isoB) as components of a butanol-acetone (BA) mixture on spray, combustion, engine performance and emission characteristics. The macroscopic spray characteristics including spray penetration, spray cone angle and spray volume of n-/iso-BA-diesel blends were measured at two injection pressures 300 bar and 500 bar. A direct visualisation technique high speed camera was used to analyse the images that were obtained. The spray results show that both n- and iso-BA-diesel blends achieved a slightly higher penetration distance compared to pure diesel, resulting in a better fuel-air distribution and mixing. Two blend ratios (10% and 20%) of iso- and n-BA-diesel blends were tested in a single-cylinder DI diesel engine at three engine speeds: 1400, 2000 and 2600 rpm at full load. The engine performance included measuring the following parameters: pressure inside the combustion cylinder; brake power (BP); and brake specific fuel consumption (BSFC). The exhaust gas emissions included measuring the following parameters: exhaust gas temperature (EGT); oxide of nitrogen (NO_x); unburnt hydrocarbons (UHC); carbon monoxide (CO); and carbon dioxide (CO_2). The results from the blended diesel with iso- and n- BA were also compared to pure diesel as a baseline. The results for 10 iso-BA-90 diesel showed a slight improvement in BP by 4% at medium speed, while the BP of 20iso-BA-diesel, 10 and 20 n-BA-diesel was slightly lower and comparable with pure diesel at all engine speeds. The highest peak in-cylinder pressure was measured for the iso-BA-diesel blends. BSFC and BTE were increased for both iso- and n-BA-diesel blends. CO emission reduced with the increase in both n-BA and iso-BA ratios in diesel blend. Both NO_x emissions and EGT were decreased at all n-BA and iso-BA-diesel blends compared to pure diesel. UHC and NO_x emissions concentration of n-BA-diesel blends were lower compared to that of the iso-BA-diesel blend. Thus, it can be concluded that iso-BA-diesel blends showed slight improvement in brake power and higher in-cylinder pressure, while n-BA-diesel blends resulted in lower emission levels in regard to NO_x and UHC. Therefore, using n-BA and iso-BA blended together as an additive for diesel fuel could be a suitable blend to obtain optimum results in regard to engine performance.

1. Introduction

Exhaust emissions from diesel engines raise significant concerns for two reasons: they have a negative impact on both human health and climate change [1,2]. Fuel consumption and demand have significantly increased in the last few years due to population growth. Therefore, using alcohol as additive for conventional diesel is a good option to reduce depending on fossil fuel and reduce emission levels. Using a high-alcohol biofuel chain that consist of four or more carbon atoms such as butanol (C_4) could potentially diminish emissions [3]. Butanol has more advantages compared to lower-chain alcohols such as ethanol: (1) less corrosive behaviour

---

[*] Corresponding author.
E-mail address: Sattarjabbarmurad.algayyim@usq.edu.au (S.J.M. Algayyim).

https://doi.org/10.1016/j.energy.2017.09.044

Nomenclature

Symbol	
ABE	acetone-butanol-ethanol mixture
BA	butanol-acetone mixture
B20D80	20% butanol 80% diesel
10n-BA90D	10% normal-butanol-acetone 90% diesel
20n-BA80D	20% normal-butanol-acetone 80% diesel
10iso-BA90D	10% iso-butanol-acetone 90% diesel
20iso-BA80D	20% iso-butanol-acetone 80% diesel
B40D60	40% butanol 60%diesel
BMEP	brake mean effective pressure
BSFC	brake specific fuel consumption
BP	brake power
BTE	brake thermal efficiency
CAD	crank angle degree
CI	compression ignition
CCD	charge-coupled device
CO	carbon monoxide
CO_2	carbon dioxide
CN	cetane number
CVV	constant-volume vessel
C_p	specific heat at constant pressure
C_v	specific heat at constant volume
DI	direct injection
DOC	diesel oxidation catalyst
EGR	exhaust gas recirculation
E10	10% ethanol 90% gasoline
EGT	exhaust gas temperature
IC	internal combustion
HVO	hydrotreated vegetable oil
HRR	heat release rate
LPG	liquefied petroleum gas
isoB	iso-butanol
MFB	mass fraction burnt
NO_x	nitrogen oxides
nB	normal butanol
PM	particulate matter
rpm	revolutions per minute
S	spray tip penetration
SecB	secondary butanol
SOI	start of injection time
THC	total hydrocarbon
TDC	top dead centre
TertB	tertiary butanol
T	torque
V	spray volume
ϕ	equivalence ratio
γ	ratio of specific heats
θ	spray cone angle

on fuel injection systems because the hygroscopic nature is lower; (2) higher flash point which means it is a safer option for storage and distribution; (3) lower vapour pressure, thus producing less evaporative emissions [4]; (4) can be produced from crop waste, reducing dependence on fossil fuel [5] and (5) All higher alcohols (more than C4) are more solubility with diesel at any blend ratio and also used as co-solvent to stabilise ethanol in diesel blend [6]. Butanol production via biotechnology processes originated in the 1900s [7,8].

The product was named ABE fermentation with different product such as acetone-(iso-butanol/n-butanol)-ethanol (ABE) [9], and (2) iso-propanol instead of acetone as (IBE) [10,11]. (3) Another study produced n-butanol/iso-butanol-acetone without ethanol as (BA) mixture [12] (Fig. 1).

According to Fig. 1, all ABE fermentation product has butanol. Butanol's structure has carbon atoms classified in two chains: straight and branched and also divided to four different isomers: normal butanol (n-butanol), secondary butanol (sec-butanol), iso-butanol and tertiary butanol (tert-butanol). All butanol isomers can reduce exhaust emission levels because they possess high oxygenated contents and low hydrocarbon mole fractions. However, the option of using sec-butanol and tert-butanol as future biofuels is unclear because their production processes are not yet established in the bio butanol industry [13]. Therefore, researching iso-butanol and n-butanol as potential additive fuels is an emerging research area. Many studies have already addressed commercial solutions to increase the yield of n-butanol and iso-butanol from fermented biomass [14–23].

In the literature review below focuses on iso-butanol and n-butanol as additive for CI engines. So these studies have been summarised and evaluated relating to the impact of using pure n-butanol or iso-butanol as a sole fuel or mixed with another fuel such as diesel at different ratios. Parameters such as blend solubility [6], spray and combustion characteristics, engine performance and exhaust gas emissions of CI engine have been considered.

Fundamental studies on blend solubility, spray characteristics [24,25] and combustion behaviour of n-butanol have been conducted including: oxidation [26,27]; laminar burning velocities [28–33]; flame structure [34–36]; ignition delay [37–39]; and soot formation [40]. In regard to iso-butanol, similar studies have been

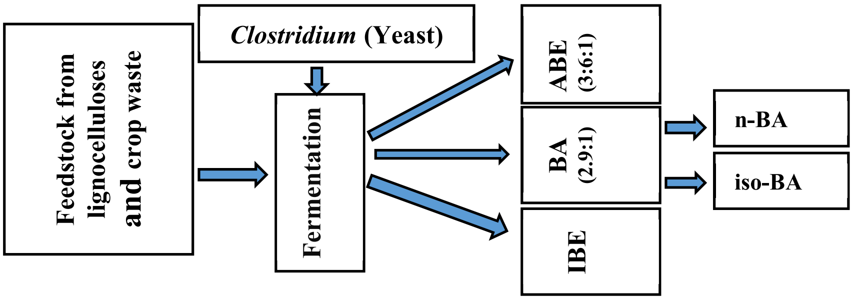


Fig. 1. BA production processes [12].

conducted [29,30,41,42]. In addition, different operating condition used and utilising various combustion strategies such as two injection stage and high EGR rate [43]. These studies demonstrated the following: (1) n-butanol (straight chain) has better soluble capacity than that of iso-butanol (branched structure) [6] (2) the spray penetration of the butanol-diesel blend was deeper as a result of its low viscosity and surface tension. However, Liu et al. [25] found that the transient liquid penetration length of n-butanol-biodiesel blend was less impact by the downstream flame and was shorter than that of biodiesel blend under same operation condition (high ambient condition), (3) the ignition delay increased with butanol content increments in the blends as a result of their lower cetane number; (4) the ignition delay time of iso-butanol was shorter compared with n-butanol under the same operating conditions [41]; and (4) the flame speed of n-butanol was higher than that of iso-butanol because it has different C–H position bonds [30]. Compared to iso-butanol, n-butanol has been more widely investigated in the last few years in CI engines to evaluate engine performance and emission levels [44–58]. In contrast, there are fewer studies related to iso-butanol [59,61]. These studies showed: (1) the maximum heat release rate and peak in-cylinder pressure increased with butanol addition as a result of enhancing fuel-air mixing caused by the long ignition delay time of the alcohols [45,46]; (2) iso-butanol has a higher peak cylinder pressure than n-butanol [61,62]; and (3) iso-butanol has the lowest soot formation [63].

In summary of all these investigations regarding the impact of n-butanol and iso-butanol blends on engine performance and emission levels, there are varying results due to various blend ratios and different operating conditions used such as a wide range of exhaust gas recirculation (EGR) rates [64]. To conclude, some general results: (1) BTE generally increased as a result of increase n-butanol content, while increase in BTE of iso-butanol was only found with low butanol ratio less than 10%; (2) NO_x emissions were decreased with iso-butanol; (3) smoke emissions were decreased with increased butanol content; and (4) HC emissions were increased with increased iso-butanol, while they were decreased with n-butanol. Table 1 summarises literature in the n-butanol and iso-butanol utilisation as blends of diesel engines.

According to review studies above, thses studies support the claim that butanol has more advantageous of CI engines as additive blend however, the main issue limitation used it in diesel engine is high production cost. Because, the high cost recovery of butanol from ABE or BA mixture consumes about 30–40% of butanol production budgets [71]. Thus, using BA as a mixture is a better way to reduce the cost of the blended fuel. Compared to ABE, the absence of ethanol in the BA mixture is another advantage of BA due to the drawbacks of ethanol usage in diesel engines [72,73].

In addition, the acetone component in the BA mixture is another benefit to the blended fuel. Acetone has some advantageous chemical properties which can enhance conventional fuel efficiency. One of these properties is the boiling point temperature, which is lower than those of ethanol and butanol (Table 2). Therefore, the acetone vapour is probably ignited before other species in the blend. The experimental results also found that the acetone content of the ABE mixture is an important component because it contributes to advancing the combustion phasing [74]. While there are many fermentation techniques that can control the final type of butanol isomers in BA fermentation, all studies have focused on using n-butanol-diesel or iso-butanol-diesel blends with diesel separately, as reported earlier, with various results. However, to best of author's knowledge, using a mixture of n-butanol or iso-butanol as components of the BA mixture with diesel in spray characteristics and CI engine performance has not been investigated. Before investigating the engine performance of both BA blends in diesel engines, spray characteristics should be understood because fuel spray significantly affects air-fuel mixing and it has a direct impact on the engine performance power and emission levels. Therefore, the goal of this study is to compare the usage of either iso-butanol or n-butanol in a BA mixture blended with pure diesel. The parameters that were studied were spray characteristics, combustion characteristics, engine performance and exhaust emission levels. This can inform the BA fermentation industry about the type of butanol they should produce.

Table 1
Summary of literature in the n-butanol and iso-butanol utilisation as blends of diesel engines.

Fuel Type	Main Findings	Reference
n-butanol	↑ ignition delay time ↑ NO_x at high load	Yanai et al. [45]
20 n-butanol & diesel	↑ ignition delay time & ↑ mixing time ↓ smoke	Valentino et al. [46]
5, 10 & 20 n-butanol & diesel	↓ Soot while ↑ HC. CO & NO_x similar to diesel	Siw et al. [47]
5,10 & 15 & 20 n-butanol & diesel	↓ Smoke opacity significantly with ↑ the butanol ratio, ↓ NO_x slightly, CO & EGT ↑ BSFC & BTE	Dogan et al. [49]
4 & 8 propanol & 4 & 8 n-butanol	↑ BTE. ↓ NO & CO,↓ Smoke density with high ratio of butanol	Balamurugan & Nalini [50]
5, 10, 15 & 20% iso-butanol	↑ BTE slightly up to 10% iso-butanol whereas it significantly ↓ with the blends containing 15 and 20% iso-butanol ↑ BSFC, CO & ↓ NO_x while ↑ HC	Karabektas, & Hosoz [59]
10, 20, 30 & 40% iso-butanol & diesel	↑ BSFC as result of the ↑ engine speed ↓ Air fuel ratio & BTE.	Al-Hasan et al. [60]
15 & 30 iso-& n-butanol & diesel	ignition delay time of n-butanol higher than iso-butanol iso-butanol has a higher peak cylinder pressure than n-butanol	Gu, X. et al. [62]
8, 16, 24 n-butanol & diesel	↓ Smoke, CO & EGT while ↑ HC ↑ BSFC, BTE a little	Rakopoulos et al. [53]& [54]
n/iso-butanol &diesel	↓ Soot and CO. ↑ NO	Zhang et al. [65]
n-butanol & diesel	↓ Soot & CO constant impact of NO_x without concern impact on BSFC	Yao et al. [66]
n-butanol	high in cylinder pressure and pressure rise rate of pure butanol	Jeftić et al. [67]
5, 10 & 20 n-butanol & diesel	↑ BSFC with ↑ butanol ↑ HC & NO while ↓ CO & PM	Mitt et al. [68]
5 n-butanol & diesel	BSFC unaffected	Zoldy et al. [69]
20 n-butanol	↓ 5% in BSFC. ↓ NO_x by 25% & ↓ CO_2 by 10%	Dobre et al. [70]

↑ = increase and ↓ = decrease.

Table 2
Properties of alcohols and diesel [62,75,76].

Properties	Acetone	iso-butanol	n-butanol	Diesel
Chemical formula	C_3H_6O	C_4H_9OH	C_4H_9OH	C_{12}–C_{25}
composition (C, H, O) (mass %)	62,10.5, 27.5	65,13.5, 21.5	65,13.5, 21.5	–
Oxygen content, mass %	27.5	21.5	21.5	0.0
Density (kg/L)	0.971	0.802	0.810	0.82–0.86
Viscosity (mm^2/s) at 40 °C	0.35	2.63	2.22	1.9–4.1
Calorific value (MJ/kg)	29.6	33.3	33.1	42.8
Cetane number	–	<15	17–25	48
Flash point (°C)	17.8	28	35	74
Boiling point (°C)	56.1	108	118	210–235
Latent heat of vaporisation (kJ/kg)	501.1	566	582	270
Surface tension	22.6	–	24.2	23.8
Auto-ignition temperature (°C)	560	415	385	≅300

Table 3
Properties of fuels tested.

Properties	Density (kg/L)	Kinematic viscosity (mm^2/s)	Lower heating value (MJ/kg)
n-BA10D90	0.835	2	41.1
n-BA20D90	0.832	1.81	39.1
iso-BA10D90	0.837	2.21	41.5
iso-BA20D90	0.833	1.9	40.2

2. Fuel preparation and properties

Butanol refers to alcohols chained with a four-carbon structure. Butanol isomers have been classified depending on the hydroxyl (OH) position in the carbon chain and are defined as n-butanol $CH_3CH_2CH_2CH_2OH$, iso-butanol $(CH_3)_2CH_2CHOH$, sec-butanol $CH_3CH_2CHOHCH_3$ and tert-butanol $(CH_3)_3COH$. The n-butanol and iso-butanol chain structures are different: n-butanol has a straight chain, but the OH group of iso-butanol is attached to an internal carbon. Through butanol fermentation production from biomass, n-butanol and iso-butanol are produced depending on fermentation techniques. In this investigation, the n-butanol, iso-butanol and acetone were 99.8% analytical grade and were obtained from Chem-Supply Australia while diesel was obtained from a local Toowoomba (Australia) petrol station. The butanol-acetone mixture was prepared with a ratio of 2.9:1 B:A, which was used to simulate the intermediate production of BA industry fermentation [12]. They were mixed with two types of butanol: either iso-butanol or n-butanol each one blended with acetone separately using splash blending. Once this was completed different volumetric blends with pure diesel were formed: 10% and 20% nBA, 10% and 20% isoBA, referred to as 10nBA90D, 20nBA80D, 10isoBA90D and 20isoBA80D. Miscibility and stability of isoBA-diesel and nBA-diesel blends were monitored over a one-month period before the tests were carried out on the engine. The samples were stored in glass bottles and visually observed every week, with all blends maintaining a good homogeneous mixture. The density was measured using volumetric and weight measurements for all fuel blends at 20 °C room temperature. The viscosity (kinematic viscosity at 40 °C) of the blend was measured using a Brookfield viscometer. The heating values of the blends were measured using a digital oxygen bomb calorimeter measured in the University of Southern Queensland lab. Each test was carried out in triplicate. Table 2 shows the properties of diesel, acetone, iso-butanol and n-butanol. Table 3 shows the measured properties of the fuel blends.

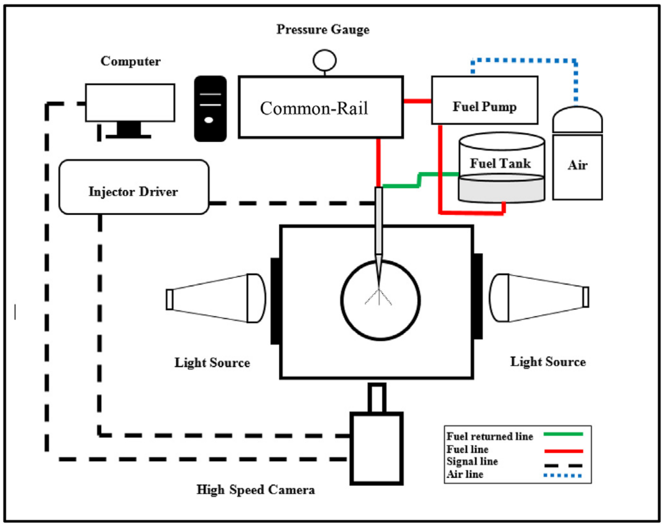


Fig. 2. Schematic of the CVV with common rail fuel injection system setup with CCD.

3. Experimental apparatus

3.1. Spray test setup

The spray characteristics test was carried out on a constant-volume vessel (CVV), at atmospheric pressure and room temperature conditions. The vessel was equipped with four windows of 93 mm diameter. Lights were installed on three of the windows and a high-speed camera on the fourth window for the purpose of spray visualisation. The inside of the vessel was painted black to ensure a good background for the images and to increase the images' contrast and enhance the visibility of the spray. The injector was mounted horizontally in the vessel so that all the spray axes are visualised through the front window.

3.1.1. Common-rail injection system

An air-driven high pressure fuel pump was used in the fuel injection system, where the fuel can be pressurised in a common-rail system. The fuel system contains the following: (1) HH701 Hartridge-type air-driven pump injector; (2) injector driver BST203-C; (3) solenoid Bosch-type injector with 0.18 mm for each hole with six holes having an injection angle of 156° connected by a common rail (Fig. 2). Moreover, two different injections of 300 bar and 500 bar were used to investigate spray characteristics, with the limitation that the engine used in the experimental test was equipped with mechanical injectors. Table 4 summarises the specifications of the injector driver fuel pump, injector and injection setup.

3.1.2. Spray image acquisition system

A Photron Charge-Coupled Device (CCD) camera was used to capture the spray blend images. The camera has a resolution of 1024 × 1024 pixels, using a capturing speed of 5000 frames per second (fps). The shutter speed and frame rate were fixed at 1/5000 s. The camera was synchronised with the injector by using the same triggering signal. A Nikon AF Micro-Nikkor lens with a focal length of 60 mm and a maximum aperture of f/2.8D with filter size 62 mm was connected to the camera. A compact solid LED light was used for illuminating the fuel spray on each window to ensure constant background light for the camera. The schematic of the injection system setup including visualisation devices is shown in Fig. 2.

Table 4
Specification of injector driver BST203-C, fuel pump, injector and injection setup.

General Specification of Injector Driver BST203-C	
Brand name	BST203-C
Net-Weight-	7.5 kg
Width × length	28.5 cm × 32.5 cm
Power	300 W & 220 V
General Specification of Fuel Pump HH701, Contains An Air-Driven High Pressure	
Net Weight	42 kg
Electricity supply	100-240 V AC 47–63 Hz
Air supply	3–6 bar
Pressure injection range	200–500 bar
Injector Makes/Type	**Solenoid**
Injection type	Bosch electromagnetic common rail injectors solenoid type
Number of nozzles	6- holes
Nozzle diameter (nominal/measured)	0.18 mm.
Injection Setup	
Injection Pressure (bar)	300–500
Start of injection time (SOI) (mm)	0.5–2.5
Injection angle (degree)	156
Injection quantity (mg)	12
Fuel temperature (°C)	23.5
Room temperature (°C)	24.8
Ambient pressure (bar)	Atmospheric pressure measured (0.949)
Test fuels	Pure diesel, 20-iso-BA-80diesel & 20n-BA-diesel

3.1.3. *Spray test conditions*

Spray characteristics of three fuel blends, pure diesel (100%), 20isoBA-80diesel blend and 20nBA-80diesel blend were investigated. Two injection pressures were tested (300 bar and 500 bar). The after start of injection time (ASOI) were 0.5, 0.75, 1, 1.5 and 2 ms. The tests were carried out at atmospheric conditions. Room temperature, fuel temperature and ambient pressure were measured. The fuel injection pump was driven with 6 bars air pressure. Table 4 presents all spray test conditions. For each fuel test, the fuel tank and fuel system line (common rail and pipes) were cleaned and emptied and the fuel filter was replaced with a new one. After ensuring all the injection systems were cleaned and emptied, the spray testing started with some preliminary injection tests for at least 5 min before recording the new images. Then, three images were taken and spray characteristics were averaged at the same elapsed time to minimise experimental errors. A program was written in MATLAB which was used to measure the two spray characteristics of spray images: spray penetration and spray angle. The captured images were converted into binary images for subtraction to remove any artefacts of background light such as those shown in Fig. 3. After that, the images were processed for further spray characteristic analysis and provided the spray tip penetration and spray cone angle. Fig. 4 showed image processing flowchart. The definition of spray tip penetration is the distance between the nozzle tip and the maximum outer point of each spray [77,78]. The spray cone angle is the angle between two straight lines from the nozzle tip and the outer contour of the injected spray [82]. Spray volume can be calculated as a function of spray penetration (S) and spray cone angle (θ) [79].

$$V = \left(\frac{\pi}{3}\right)\boldsymbol{S}^3\left[\tan^2(\boldsymbol{\theta})\right]\frac{1+2\mathbf{tan}\left(\frac{\theta}{2}\right)}{\left[1+\mathbf{tan}\left(\frac{\theta}{2}\right)\right]^3} \tag{1}$$

3.2. *Engine test setup*

The experimental test was conducted using a single cylinder, four stroke, water-cooled, direct injection (DI) diesel engine. An electrical dynamometer connected to the engine was used to control the load. The crank angles were measured using a crank angle

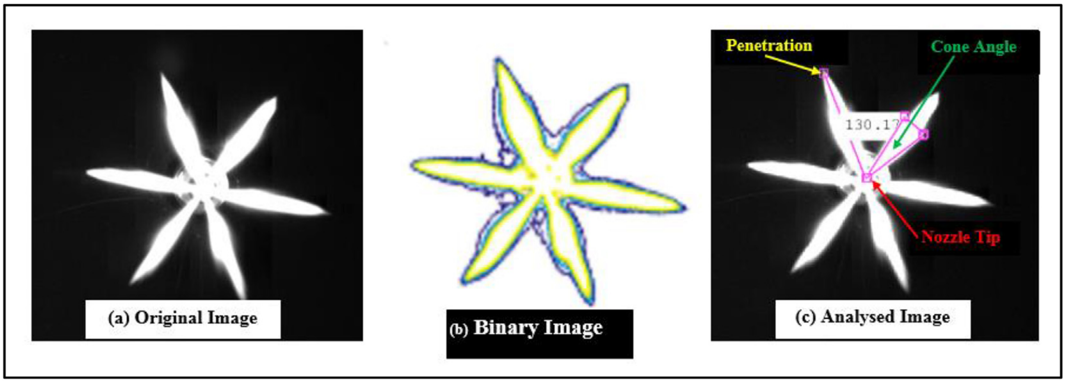

(a) Original Image
(b) Binary Image
(c) Analysed Image

Fig. 3. Procedures of image processing and macroscopic spray characteristics definitions (a) original image read in MATLAB, (b) binary image for subtraction to remove any artefacts of background light and (c): image with spray measurement.

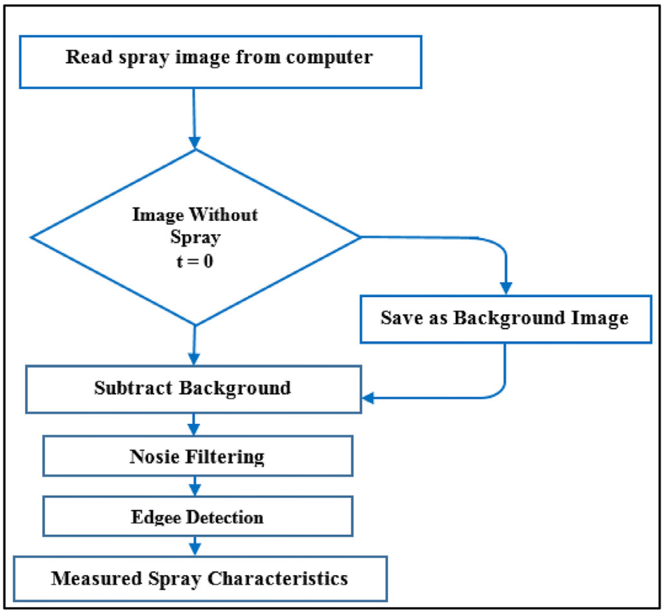


Fig. 4. Image processing flow chart.

encoder set up on the shaft of the engine. A Kistler 6052C pressure transducer (CT400.17) and charge amplifier connected to a data acquisition system with software (CT 400.09) were used to record cylinder pressure values at 1 crank angle resolution for 50 cycles each test. Table 5 contains the engine specifications.

3.2.1. *Exhaust gas analysers*

The exhaust gas emission was analysed using the Coda gas analyser to measure oxides of nitrogen (NO_x), unburnt hydrocarbon (UHC), carbon dioxide (CO_2) and carbon monoxide (CO). The accuracy ranges of the Coda gas analysers are 0.1% O_2, 0.1% CO_2, 10 ppm NO_x, 10 ppm UHC and 0.01% CO. The accuracy ranges of the other equipment are: thermocouple in the exhaust manifold, 0.0001 °C; pressure transducer in cylinder head, 0.000001 bar; fuel flow, 0.0001 L/h; tachometer on the output shaft; 0.0001 rpm; and load cell on dynamometer 0.0001 Nm.

3.2.2. *Engine test conditions*

The engine was heated up until steady-state conditions were reached. The experiments started with testing pure diesel (D100), then the different blends: 10iso-BA90D, 20iso-BA80D, 10n-BA90D and 20n-BA80D. The experiments were carried out in triplicate to assess the experimental error. When new fuel was tested, the fuel system was emptied and cleaned with a vacuum pressure pump to remove all the old fuel that was in the injection system. In addition, after that, the engine was filled with a new fuel and operated for at least 20 min before recording commenced to get a sufficiently stable operating condition. The engine tests were conducted at engine speeds of 1400, 2000 and 2600 rpm and at the same compression ratio 19:1 in all experiments with full load.

Table 5
Engine specifications.

Engine manufacturer	Farymann
Engine model	G.U·N.T. Hamburg
Combustion type	Direct Injection Engine
Number of cylinders	1
Compression ratio	5:1–19:1
Maximum power (kW)	Approx. 6 kW
Speed range (rpm)	900–3000
Bore	90 mm
Stroke	74 mm
Capacity	470 cm^3
Maximum compression pressure	60–80 bar
Nozzle injection pressure	300 bar
Injection type	Direct Injection
Exhaust closes	4.5 … 6.7° ATDC
Inlet opens	5.2 … 7.5° BTDC

3.2.3. *Heat release rate (HRR) formulation*

The heat release rate was calculated from the cylinder pressure data and crank angle readings that were recorded in the data acquisition of each test. The analysis was derived from the first law of thermodynamics for a closed system with an ideal gas after the compression stroke before the exhaust valve opens [80].

$$\frac{dQ_n}{d\theta} = \frac{\gamma}{\gamma\text{-}1} P \frac{dV}{d\theta} + \frac{1}{\gamma\text{-}1} V \frac{dP}{d\theta} = \left(\frac{\gamma}{\gamma\text{-}1} \times P_I \times (V_{i+1}\text{-}V_i) + \frac{1}{\gamma\text{-}1} \times V_I \times (P_{i+1}\text{-}P_i) \right) \Big/ \Delta\theta$$

here: $dQn/d\theta$ is the heat release rate per crank angle (CAD), $\gamma = C_p/C_v = 1.35$ is the ratio of specific heats. The input values are the pressure data (collected as function of crank angle) and the cylinder volume V at any crank angle θ (calculated from the engine geometry).

4. Results of spray characteristics and discussion

Spray macroscopic characteristics of pure diesel, 20isoBA-diesel and 20nBA-diesel under various injection pressures were obtained using high-speed camera. Fig. 5 illustrates the spray image evolution. After start of injection (ASOI) refers to the time interval between injection signal and actual injection event (the first appearance of liquid on the images). When ASOI was zero, the image was stored as a background image used in the analysis of the images in Fig. 5 by subtraction to remove any artefacts of background light.

4.1. *Spray tip penetration*

Spray tip penetration of pure diesel, 20%nBA-diesel and 20%iso-BA-diesel blends at two injection pressures (300 bar and 500 bar) under different after start of injection (ASOI) (0.5 ms, 0.75 ms, 1 ms, 1.5 ms and 2 ms) is presented in Fig. 6. It is observed from the figures that both n- and iso-BA-diesel blends showed slight improvement of spray penetration depth at both injection pressures due to the low viscosity and surface tension of the alcohol blend compared to that of pure diesel (Table 2). In addition, the spray penetration of the n-BA-diesel blend was slightly higher than that of the iso-BA-diesel blend due to n-butanol having lower viscosity compared to iso-butanol. Improvement in spray penetration can improve air-fuel atomisation and result in better reactions. In addition, increasing injection pressure resulted in deeper spray liquid penetration. These results are consistent with Refs. [81–83]. Greater penetration along with high swirl ratio and hot walls results in proper combustion. Many studies support the claim that increasing the injection pressure is more advantageous in regard to improving engine performance and reducing exhaust emissions [84,85]. It is well known that higher injection pressure forces the liquid fuel to leave the nozzle within turbulent flow, assisting the outer boundaries of the sprayed fuel to break up into droplets. In general, increasing the injection pressure leads to advancing the start of combustion due to improved atomisation which results in

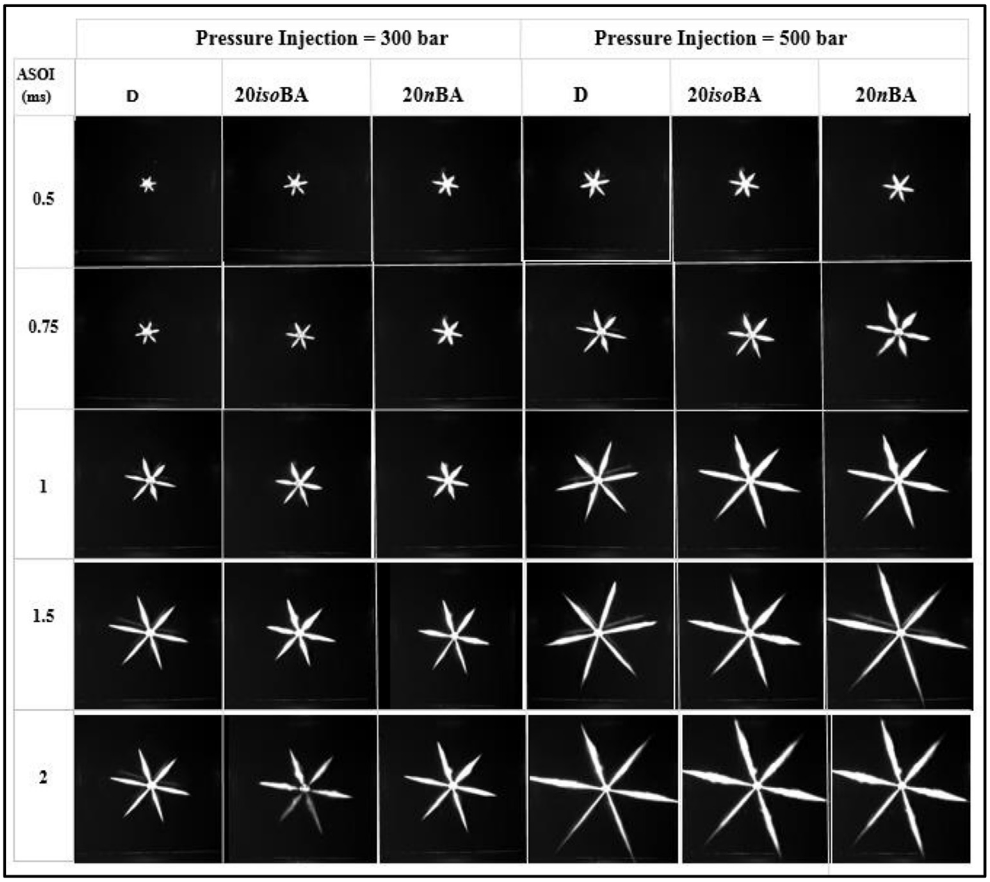


Fig. 5. Spray comparison images of pure diesel, 20iso-BA-diesel and 20n-BA-diesel blends using Bosch injector with 0.18 mm hole diameter with two injection pressures 300 bar (left) and 500 bar (right). Rows are (from top to bottom) ASOI of 0.5 ms, 0.75 ms, 1 ms, 1.5 ms and 2 ms.

better air-fuel mixing. In contrast, less spray penetration may lead to improper mixing rate and poor air utilisation which leads to high emissions. Thus the spray penetration is an important factor in deciding the engine emissions. Table 6 presents the standard deviation of spray tip penetration at injection pressures of 300 bar and 500 bar of all fuel blends.

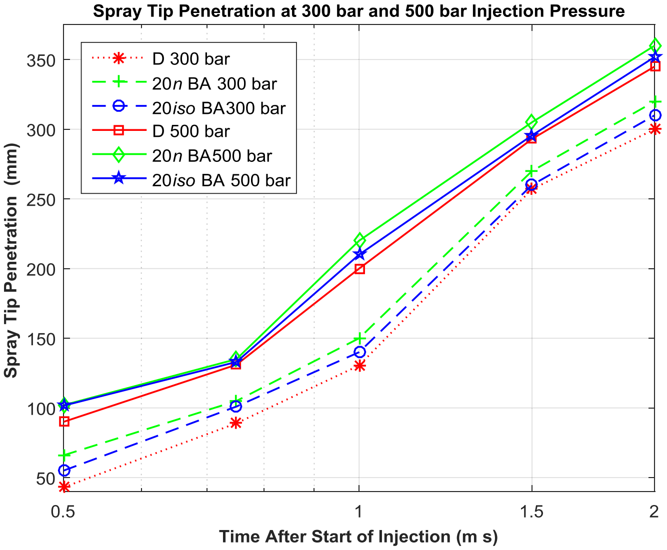


Fig. 6. Spray tip penetration for different fuel blends.

4.2. Spray cone angle and spray volume

Fig. 7 illustrates the spray cone angle of the test blends. The spray cone angle was not changed significantly via the increment in injection pressure, consistent with Delacourt et al. [79] who also investigated the impact of injection pressure on the spray penetration and cone angle at ambient temperature. Their results showed that the spray cone angle was affected slightly by injection pressure and remained nearly constant during the entire injection process [79].

Fig. 8 shows the relation between spray volumes calculated using (Equation (1)) for various ASOI. It is clearly noticeable that spray volume increased as a result of the advance injection pressure. A similar result was reported in Ref. [79].

5. Results of engine test and discussion

5.1. Combustion characteristics

5.1.1. In-cylinder pressure

Figs. 9–11 show cylinder pressure trace averaged for 50 engine cycles for pure diesel and 10% and 20% iso-BA and n-BA-diesel

Table 6
Standard deviation of spray tip penetration (mm) at injection pressure 300 bar and 500 bar.

Blend	Injection Pressure 300 bar	Injection Pressure 500 bar
Diesel	±1. 44	±1.52
20n-BA-diesel blend	±1.21	±1. 33
20is-BA-diesel blend	±1.32	±1.45

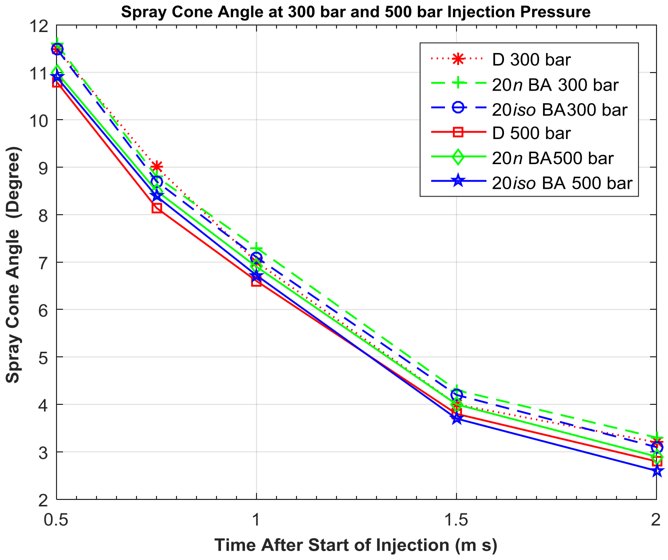


Fig. 7. Spray cone angle for different fuel blends.

blends as a function of the crank angle at different engine speeds. It can be seen from Figs. 9 and 10 that all iso-BA-diesel blends showed the maximum peak rate in-cylinder pressure compared to that of a pure diesel fuel at medium and high engine speeds. This occurs due to the low cetane number and high volatilities of iso-BA blends. The impact of the low cetane numbers of the 20iso-BA and 20n-BA led to longer ignition delay times than that of diesel fuel. According to a comparable study by Pan et al. [41] of ignition delay time between n-butanol and iso-butanol, ignition delay time of n-butanol was longer compared to that of iso-butanol [41].

5.1.2. *Heat release rate (HRR)*

Figs. 12–14 present the heat release rate of both iso- and n-BA-diesel blends at three engine speeds. It can be seen that the 20iso-BA-diesel blend presents the highest peak heat release rate at all engine speeds compared to pure diesel and n-BA-diesel blend. The peak cylinder pressure (Figs. 9–11) generally corresponds to the highest heat release rate. Similar trends were found in Refs. [62,86].

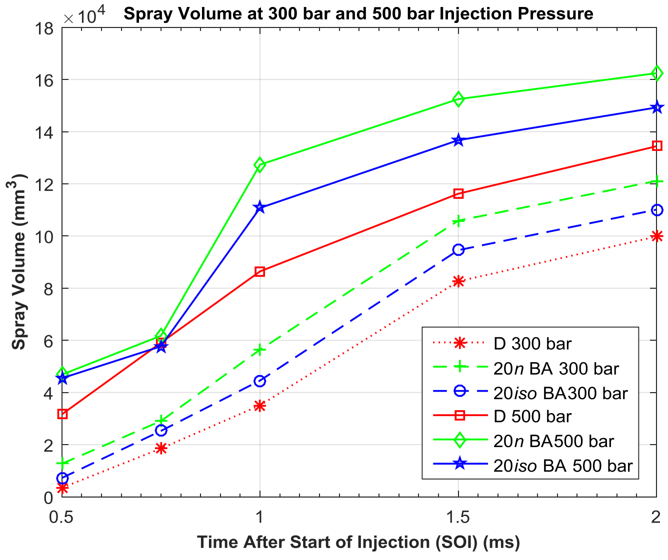


Fig. 8. Spray volume for different fuel blends.

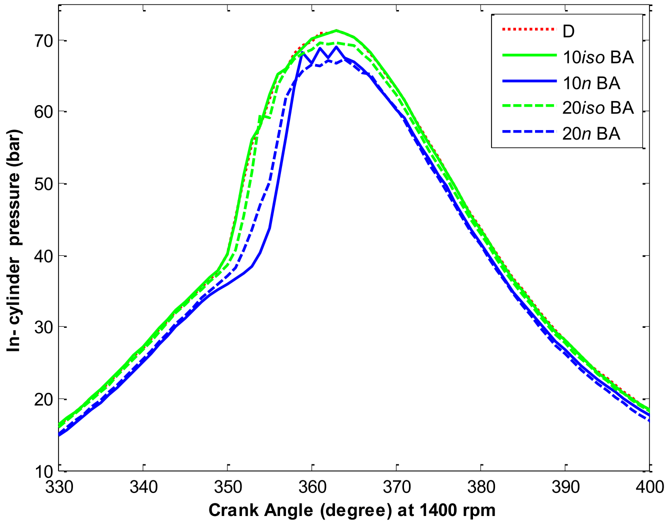


Fig. 9. In-cylinder pressure for all blends of fuel at engine speed 1400 rpm.

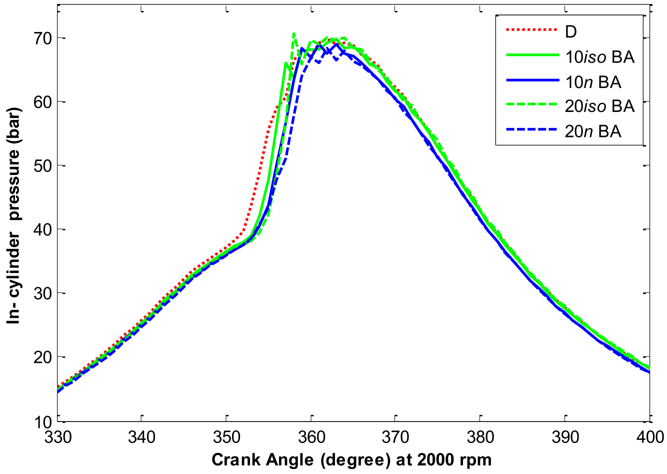


Fig. 10. In-cylinder pressure for all blends of fuel at engine speed 2000 rpm.

It is also significant that increasing the BA content delayed the maximum heat release rate. High branch of fuel also leads to a

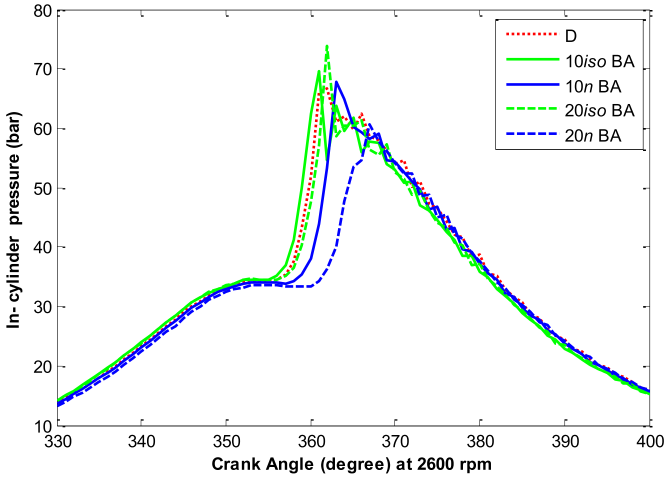


Fig. 11. In-cylinder pressure for all blends of fuel at engine speed 2600 rpm.

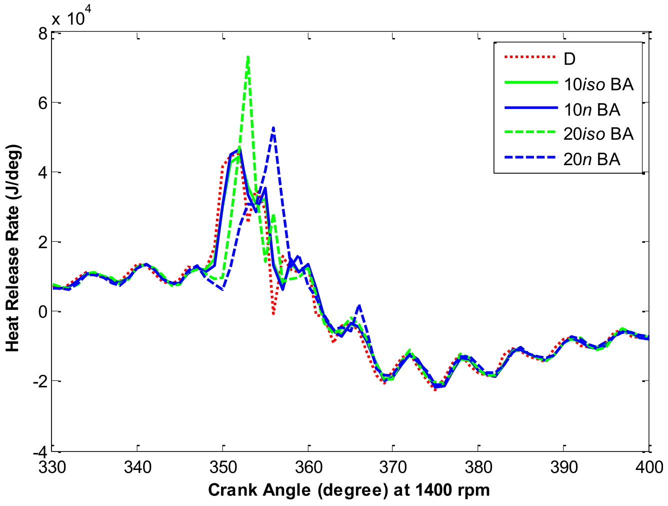


Fig. 12. Heat release rate for all blends of fuel at engine speed 1400 rpm.

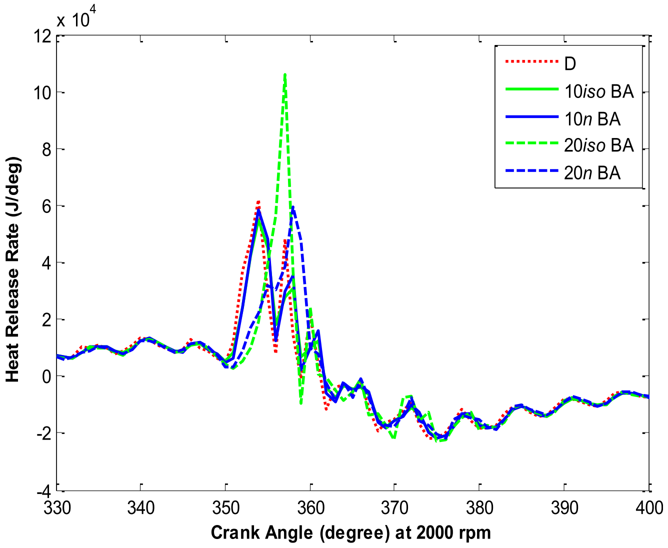


Fig. 13. Heat release rate for all blends of fuel at engine speed 2000 rpm.

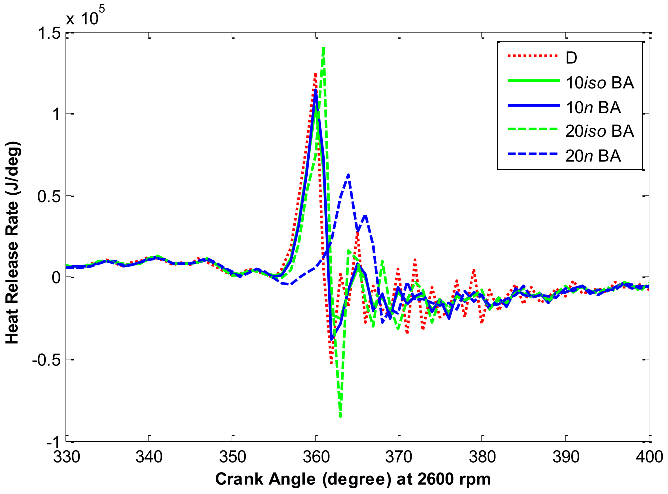


Fig. 14. Heat release rate for all blends of fuel at engine speed 2600 rpm.

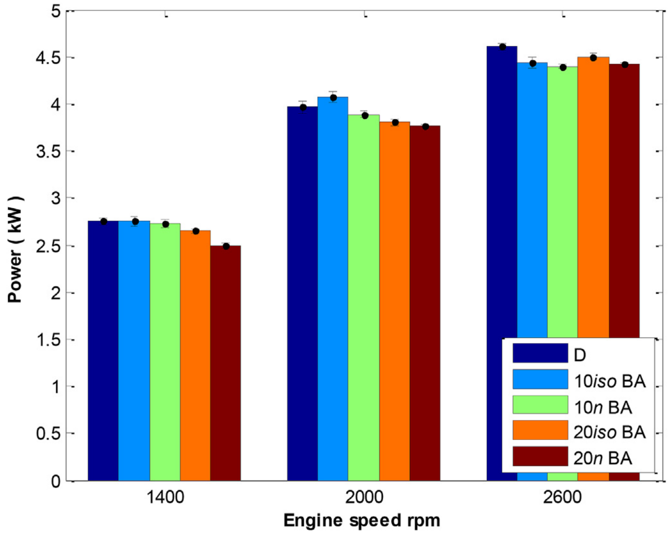


Fig. 15. Brake power for all blends of fuel at three speeds.

reduction in the flame speed of iso-butanol compared to that of n-butanol, and this results in high heat release.

5.2. Engine performance characteristics

5.2.1. Brake power and torque

Figs. 15 and 16 show the relation between BP and torque (T) at three different engine speeds at various blend ratios of iso-BA and n-BA-diesel blends. BP and T were slightly decreased for most alcohol blends compared to those of pure diesel, while 10% iso-BA-diesel presented a slight improvement in BP and torque by 4% compared to that of diesel at medium engine speed. These results are consistent with other studies [59] and are due to the lower calorific values of alcohols (Tables 2 and 3).

5.2.2. Brake thermal efficiency & brake specific fuel consumption

Fig. 17 shows the brake thermal efficiency (BTE) of iso-BA and n-BA-diesel blends and the pure diesel blend. BTE was increased for all BA-diesel blends compared to that of pure diesel at all engine

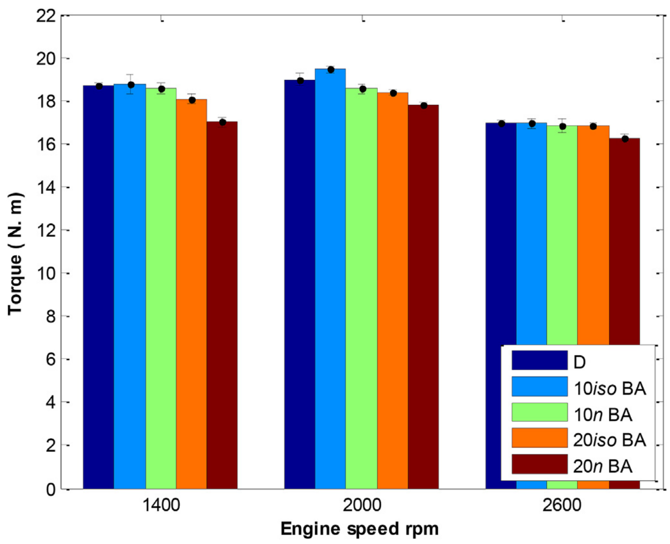


Fig. 16. Torque for all blends of fuel at three speeds.

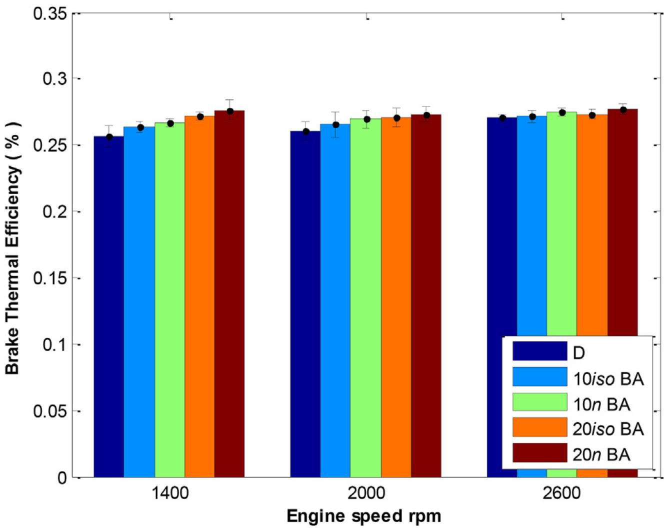


Fig. 17. BTE for all blends of fuel at three speeds.

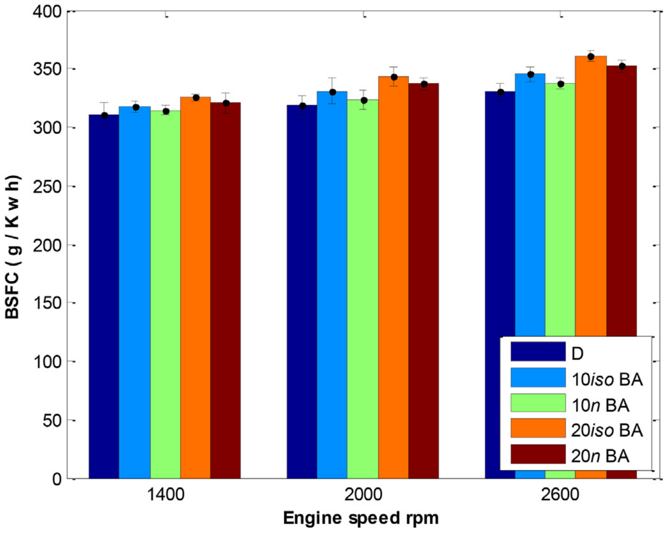


Fig. 18. BSFC for all blends of fuel at three engine speeds.

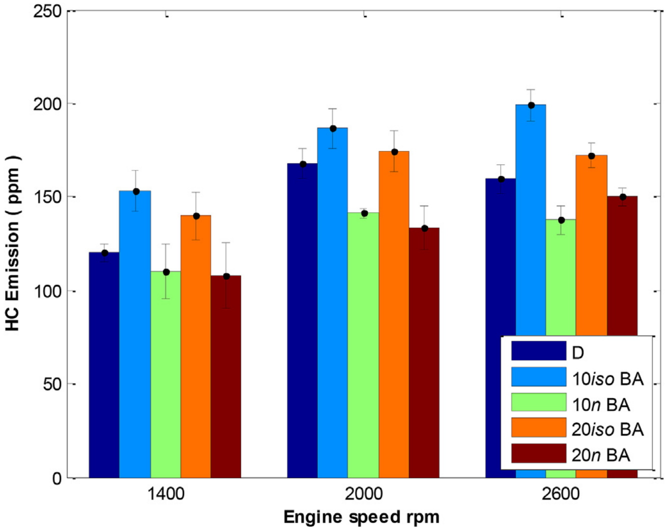


Fig. 19. UHC emissions for all blends of fuel at three engine speeds.

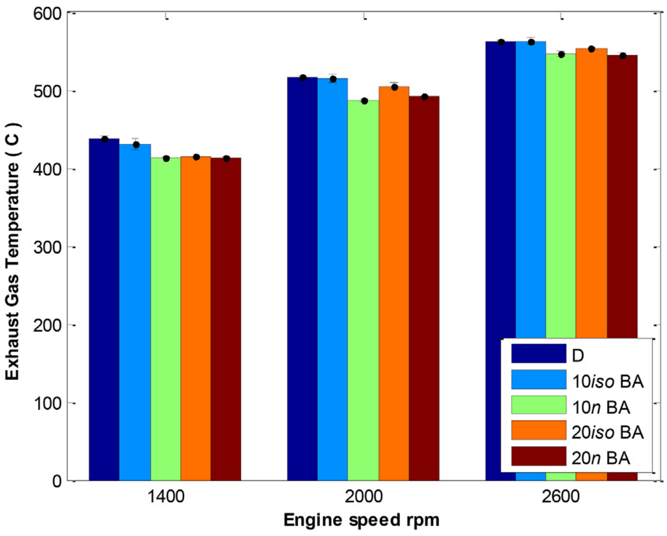


Fig. 20. EGT for all blends of fuel at three engine speeds.

speeds. Other studies have shown that alcohol/diesel blends have higher brake thermal efficiencies than pure diesel because their lower CN improves fuel/air mixing, enabling rapid energy release and increasing combustion efficiency [49,50,53,54,86]. In addition, BTE of the n-BA-diesel blends was slightly higher than that of iso-BA-diesel blends at all engine speeds due to the higher cetane number and density of n-butanol compared to iso-butanol in the BA mixture (Table 2).

Fig. 18 shows BSFC of iso-BA and n-BA-diesel blends and the pure diesel fuel. BSFC was increased for all BA-diesel blends compared to that of pure diesel at all engine speeds due to the lower calorific values of the additives. This is consistent with other studies [65,87]. In addition, iso-BA-diesel has the highest BSFC at all engine speeds, consistent with Ref [87].

5.3. Emissions characteristics

5.3.1. Unburnt hydrocarbon (UHC)

The usage of iso-BA increased the UHC compared to diesel, while n-BA-diesel produced approximately the same or less UHC than diesel Fig. 19.This is because n-butanol has a higher heat of vaporisation compared to iso-butanol (Table 2). Low viscosity also affects the spray penetration so n-BA-diesel blend presents longer or deeper spray penetration compared to that of iso-BA-diesel blends, which results in producing small droplets, more surface area contact, and enhancing air-fuel mixing, consequently increasing the overall reaction rate. However, iso-BA-diesel showed higher UHC due to the molecular chain structure where the OH group and C—H position are different to n-butanol (straight chain). The C—H bond significantly affects the reaction rate due to the different energy required for cracking the bonds or branches [30]. Terminal C—H bonds have greater or higher energy compared to inner C—H bonds [29]. In addition, the H-abstraction reaction is slower for a higher bond energy value which leads to a low overall reaction rate [29,30]. Because iso-butanol has the most terminal C—H bonds, the reaction rate of iso-butanol in BA will be lower, resulting in insufficient time to complete the reaction and cause an increase in UHC emissions. Similar findings are reported in Ref. [59]. N-butanol has the most inner C—H bonds possible, which means the reaction rate of n-butanol in BA will be higher, resulting in sufficient time to complete the reaction, and causing a decrease in UHC emissions. Similar findings are reported in Ref. [87].

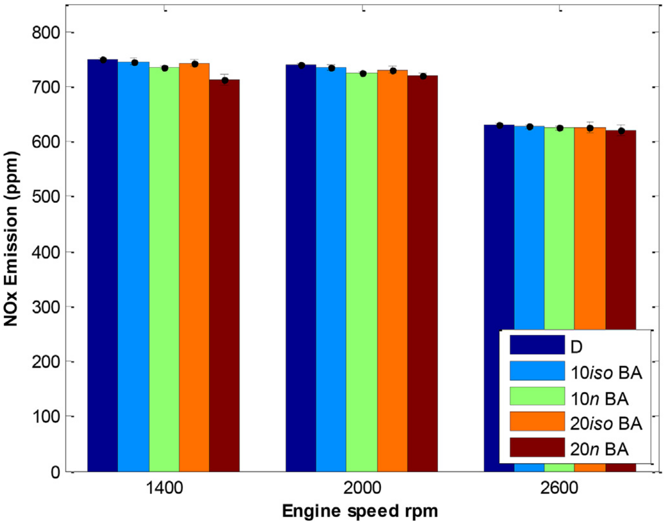


Fig. 21. NO_x emissions for all blends of fuel at three engine speeds.

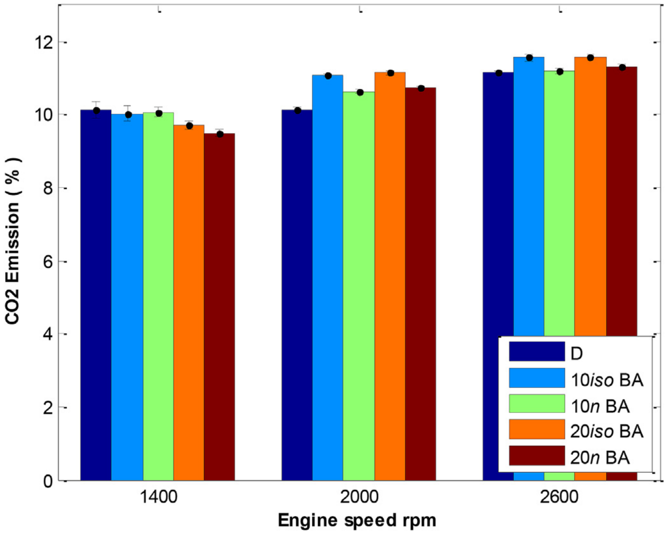


Fig. 23. CO_2 emissions of all blends of fuel at three engine speeds.

5.3.2. *Exhaust gas temperature and NOx formation*

Fig. 20 shows the relation between the exhaust gas temperatures (EGT) of test fuel at various speeds. EGT is highest for pure diesel because n-butanol, iso-butanol and acetone have much higher latent heats and lower calorific values than pure diesel fuel (Table 2). Consequently, the EGT of 20 iso-BA/n-BA-diesel blend was reduced by up to 6% compared to pure diesel. This result is consistent with the results reported in other studies [86]. In addition, n-BA-diesel has a slightly lower EGT than that of iso-BA-diesel because its latent heat of vaporisation is slightly higher than iso-butanol (Table 2).

Fig. 21 shows the relation between NO_x emissions of iso-BA and n-BA-diesel blends and pure diesel at different engine speeds. It was observed that pure diesel gave the highest NO_x emission at all engine speeds because of its higher combustion temperature and lower oxygen content. These results were consistent with results reported in other studies [49,59,87]. N-BA-diesel gives lower NO_x emission than that of iso-BA-diesel blend and pure diesel by 6% due to the higher cetane number of n-butanol. Moreover, n-butanol had higher flame speeds than that of iso-butanol resulting in decreased NO_x emissions [26,30].

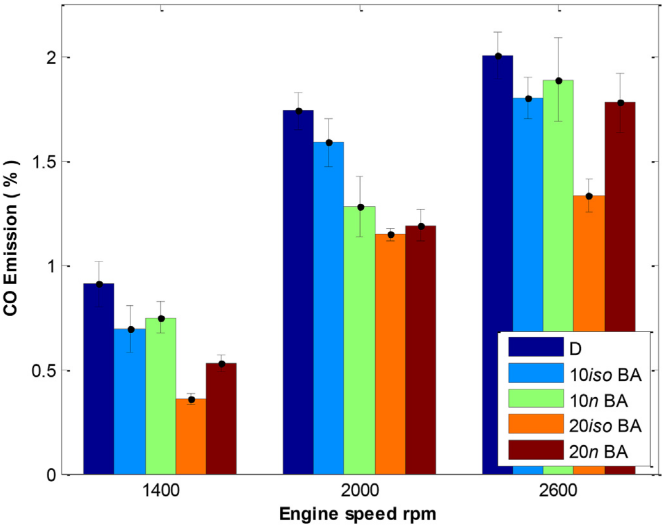


Fig. 22. CO emissions for all blends for fuel at three engine speeds.

5.3.3. *Carbon monoxide (CO) and carbon dioxide (CO2)*

Fig. 22 shows CO emissions for the tested fuels. It was observed that increasing the BA content substantially reduced the CO emissions at all engine speeds due to the higher oxygen content in both butanol blends. CO emissions of iso-BA-diesel blends were lower than that of the equivalent n-BA-diesel blend for most conditions. The maximum reduction of CO emission was seen for 20iso-BA-diesel blends by 35%–60% compared to pure diesel.

Fig. 23 shows the corresponding CO_2 emissions which were higher for both types of butanol than that of pure diesel at medium and high engine speeds due to the improved conversion of CO to $CO_{2.}$ Interestingly, the CO_2 emissions for the alcohol fuels were lower than diesel for the lowest speed. This is because the mixture was leanest at the lowest speed (based on the total carbon content from CO and CO_2, so the 20iso-/n-BA blends must have been the leanest mixtures tested.

6. Conclusion

This experimental study revealed varying results of n-BA and iso-BA blended with diesel as a green alternative fuel. The spray experiments were conducted in CVV at atmospheric conditions using two injection pressures. The macroscopic spray characteristics of 20 iso- and n-BA diesel blends and pure diesel were measured. The engine test experiments were also carried out in a single-cylinder diesel engine. The engine performance and exhaust gas emissions between n-BA and iso-BA-diesel blend and diesel were assessed and compared. Some conclusions follow:

- Both n-BA and iso-BA-diesel blend mixtures were miscible in diesel without any phase separation at different storing temperatures.
- Spray penetration of both n- and iso-BA-diesel blends is higher than pure diesel fuel. Spray penetration of n-BA-diesel was slightly higher than that of iso-BA-diesel blend.
- BSFC was increased with the increase in n-BA-diesel blend and iso-BA-diesel blend mixture content in diesel fuel due to their lower energy content.

- The 10 iso-BA-diesel blend showed slight improvement in BP at low and medium speeds compared to that of the n-BA-diesel blend
- iso-BA-diesel presented high peak in-cylinder pressure and resulted in high heat release rate at medium and high engine speeds compared to that of n-BA-diesel and pure diesel.
- CO emission was reduced with the increase in iso-BA and n-BA-diesel blend content in diesel fuel because of the more complete combustion of CO to CO$_2$ and iso-BA-diesel blend showed much lower CO emissions than n-BA-diesel blend.
- UHC emissions were increased for iso-BA-diesel blends. However, n-BA-diesel blends have lower or comparable HC emissions to diesel due to the impact of the energy required to crack the terminal C–H of iso-butanol and inner C–H bonds in n-butanol in the BA mixture.
- EGT and NO$_x$ emissions were reduced with an increase in n-BA and iso-BA content. This is because the heat of vaporisation of all alcohols was higher which leads to a peak temperature reduction inside the combustion chamber.
- N-BA-diesel produces lower NO$_x$ emission than that of iso-BA-diesel blends.

The n-BA and iso-BA mixtures are eco-friendly alternative fuel blends produced from biomass. The intermediate fermentation product of butanol, n-BA and iso-BA mixtures should soon be given more attention as a diesel additive. These alcohols can easily blend with diesel in any percentage with no phase separation. They have less corrosion behaviour than ethanol which could be used with minor modifications in existing diesel engines in the case of blending 20% and above, but with 10% blending there is no need for any engine modifications. It can be concluded that there are some advantages of iso-BA-diesel blends in regard to higher in-cylinder pressure and brake power, while n-BA-diesel blends presents lower emission levels in regard to NO$_x$ and UHC. Therefore using n-BA and iso-BA blended together as an additive for diesel fuel could be a suitable blend to obtain optimum results in regard to engine performance and could be a good alternative as an additive fuel that soon could be utilised.

Acknowledgments

The first author thank the Iraqi Government Ministry of Higher Education and Scientific Research. The authors are also grateful to Dr Saddam Al-Lwayzy, Dr Rishabh Choudhury and Mr Robert Kimber (USQ) staff for assisting with experiments.

References

[1] Shuai C, Shen L, Jiao L, Wu Y, Tan Y. Identifying key impact factors on carbon emission: evidences from panel and time-series data of 125 countries from 1990 to 2011. Appl Energy 2017;187:310–25.
[2] Gupta RB, Demirbas A. Gasoline, diesel, and ethanol biofuels from grasses and plants. Cambridge University Press; 2010.
[3] Savaliya ML, Dhorajiya BD, Dholakiya BZ. Recent advancement in production of liquid biofuels from renewable resources: a review. Res Chem Intermed 2013;41(2):475–509.
[4] Rajesh Kumar B, Saravanan S, Rana D, Nagendran A. A comparative analysis on combustion and emissions of some next generation higher-alcohol/diesel blends in a direct-injection diesel engine. Energy Convers Manag 2016;119:246–56.
[5] Trindade WR d S, Santos R G d. Review on the characteristics of butanol, its production and use as fuel in internal combustion engines. Renew Sustain Energy Rev 2017;69:642–51.
[6] Liu H, Hu B, Jin C. Effects of different alcohols additives on solubility of hydrous ethanol/diesel fuel blends. Fuel 2016;184:440–8.
[7] Weizmann C. Improvements in the bacterial fermentation of carbohydrates and in bacterial cultures for the same. Symbiotic Assoc Biotechnol Appl Microbiol 1915:1.
[8] Jones DT, Woods DR. Acetone-butanol fermentation revisited. Microbiol Rev 1986;50(4):484.
[9] Kheyrandish M, Asadollahi MA, Jeihanipour A, Jeihanipour M, Rismani-Yazdi H, Karimi K. Direct production of acetone–butanol–ethanol from waste starch by free and immobilized Clostridium acetobutylicum. Fuel 2015;142:129–33.
[10] Ezeji TC, Qureshi N, Blaschek HP. Continuous butanol fermentation and feed starch retrogradation: butanol fermentation sustainability using Clostridium beijerinckii BA101. J Biotechnol 2005;115(2):179–87.
[11] Green EM. Fermentative production of butanol—the industrial perspective. Curr Opin Biotechnol 2011;22(3):337–43.
[12] Li X, Li Z-G, Shi Z-P. Metabolic flux and transcriptional analysis elucidate higher butanol/acetone ratio feature in ABE extractive fermentation by Clostridium acetobutylicum using cassava substrate. Bioresour Bioprocess 2014;1(1):1–13.
[13] Oßwald P, Güldenberg H, Kohse-Höinghaus K, Yang B, Yuan T, Qi F. Combustion of butanol isomers – a detailed molecular beam mass spectrometry investigation of their flame chemistry. Combust Flame 2011;158(1):2–15.
[14] Abd-Alla MH, Zohri AN, El-Enany AW, Ali SM. Acetone-butanol-ethanol production from substandard and surplus dates by Egyptian native Clostridium strains. Anaerobe 2015;32:77–86.
[15] Abd-Alla MH, Elsadek El-Enany A-W. Production of acetone-butanol-ethanol from spoilage date palm (Phoenix dactylifera L.) fruits by mixed culture of Clostridium acetobutylicum and Bacillus subtilis. Biomass Bioenergy 2012;42:172–8.
[16] Bellido C, Infante C, Coca M, González-Benito G, Lucas S, García-Cubero MT. Efficient acetone–butanol–ethanol production by Clostridium beijerinckii from sugar beet pulp. Bioresour Technol 2015;190:332–8.
[17] Yang M, Zhang J, Kuittinen S, Vepsäläinen J, Soininen P, Keinänen M, et al. Enhanced sugar production from pretreated barley straw by additive xylanase and surfactants in enzymatic hydrolysis for acetone–butanol–ethanol fermentation. Bioresour Technol 2015;189:131–7.
[18] Thang VH, Kobayashi G. A novel process for direct production of acetone–butanol–ethanol from native starches using granular starch hydrolyzing enzyme by Clostridium saccharoperbutylacetonicum N1-4. Appl Biochem Biotechnol 2014;172(4):1818–31.
[19] Qureshi N, Saha BC, Hector RE, Dien B, Hughes S, Liu S, et al. Production of butanol (a biofuel) from agricultural residues: Part II – use of corn stover and switchgrass hydrolysates. Biomass Bioenergy 2010;34(4):566–71.
[20] Jiang Y, Liu J, Jiang W, Yang Y, Yang S. Current status and prospects of industrial bio-production of n-butanol in China. Biotechnol Adv 2015;33(7):1493–501.
[21] Higashide W, Li Y, Yang Y, Liao JC. Metabolic engineering of Clostridium cellulolyticum for production of isobutanol from cellulose. Appl Environ Microbiol 2011;77(8):2727–33.
[22] Desai SH, Rabinovitch-Deere CA, Fan Z, Atsumi S. Isobutanol production from cellobionic acid in Escherichia coli. Microb Cell factories 2015;14(1):52.
[23] Ofuonye E, Kutin K, Stuart DT. Engineering Saccharomyces cerevisiae fermentative pathways for the production of isobutanol. Biofuels 2013;4(2):185–201.
[24] Wu H, Nithyanandan K, Lee TH, Lee C-f F, Zhang C. Spray and combustion characteristics of neat acetone-butanol-ethanol,n-butanol, and diesel in a constant volume chamber. Energy Fuels 2014;28(10):6380–91.
[25] Liu H, Huo M, Liu Y, Wang X, Wang H, Yao M, et al. Time-resolved spray, flame, soot quantitative measurement fueling n-butanol and soybean biodiesel in a constant volume chamber under various ambient temperatures. Fuel 2014;133:317–25.
[26] Moss JT, Berkowitz AM, Oehlschlaeger MA, Biet J, Warth V, Glaude P-A, et al. An experimental and kinetic modeling study of the oxidation of the four isomers of butanol. J Phys Chem A 2008;112(43):10843–55.
[27] Zhang J, Wei L, Man X, Jiang X, Zhang Y, Hu E, et al. Experimental and modeling study of n-butanol oxidation at high temperature. Energy Fuels 2012;26(6):3368–80.
[28] Gu X, Huang Z, Li Q, Tang C. Measurements of laminar burning velocities and Markstein lengths of n-butanol– air premixed mixtures at elevated temperatures and pressures. Energy Fuels 2009;23(10):4900–7.
[29] Gu X, Huang Z, Wu S, Li Q. Laminar burning velocities and flame instabilities of butanol isomers–air mixtures. Combust Flame 2010;157(12):2318–25.
[30] Wu F, Law CK. An experimental and mechanistic study on the laminar flame speed, Markstein length and flame chemistry of the butanol isomers. Combust Flame 2013;160(12):2744–56.
[31] Gu X, Li Q, Huang Z. Laminar burning characteristics of diluted n-butanol/air mixtures. Combust Sci Technol 2011;183(12):1360–75.
[32] Sarathy SM, Thomson MJ, Togbé C, Dagaut P, Halter F, Mounaim-Rousselle C. An experimental and kinetic modeling study of n-butanol combustion. Combust Flame 2009;156(4):852–64.
[33] Beeckmann J, Cai L, Pitsch H. Experimental investigation of the laminar burning velocities of methanol, ethanol, n-propanol, and n-butanol at high pressure. Fuel 2014;117:340–50.
[34] Oßwald P, Güldenberg H, Kohse-Höinghaus K, Yang B, Yuan T, Qi F. Combustion of butanol isomers–a detailed molecular beam mass spectrometry investigation of their flame chemistry. Combust Flame 2011;158(1):2–15.
[35] Grana R, Frassoldati A, Faravelli T, Niemann U, Ranzi E, Seiser R, et al. An experimental and kinetic modeling study of combustion of isomers of butanol. Combust Flame 2010;157(11):2137–54.
[36] Hansen N, Harper M, Green W. High-temperature oxidation chemistry of n-butanol–experiments in low-pressure premixed flames and detailed kinetic

modeling. Phys Chem Chem Phys 2011;13(45):20262–74.
[37] Zhang J, Niu S, Zhang Y, Tang C, Jiang X, Hu E, et al. Experimental and modeling study of the auto-ignition of n-heptane/n-butanol mixtures. Combust Flame 2013;160(1):31–9.
[38] Weber BW, Kumar K, Zhang Y, Sung C-J. Autoignition of n-butanol at elevated pressure and low-to-intermediate temperature. Combust Flame 2011;158(5):809–19.
[39] Heufer K, Fernandes R, Olivier H, Beeckmann J, Röhl O, Peters N. Shock tube investigations of ignition delays of n-butanol at elevated pressures between 770 and 1250K. Proc Combust Inst 2011;33(1):359–66.
[40] Singh P, Hui X, Sung C-J. Soot formation in non-premixed counterflow flames of butane and butanol isomers. Combust Flame 2016;164:167–82.
[41] Pan L, Zhang Y, Tian Z, Yang F, Huang Z. Experimental and kinetic study on ignition delay times of iso-butanol. Energy & Fuels 2014;28(3):2160–9.
[42] Hansen N, Merchant SS, Harper MR, Green WH. The predictive capability of an automatically generated combustion chemistry mechanism: chemical structures of premixed iso-butanol flames. Combust Flame 2013;160(11):2343–51.
[43] Zheng Z, Yue L, Liu H, Zhu Y, Zhong X, Yao M. Effect of two-stage injection on combustion and emissions under high EGR rate on a diesel engine by fueling blends of diesel/gasoline, diesel/n-butanol, diesel/gasoline/n-butanol and pure diesel. Energy Convers Manag 2015;90:1–11.
[44] Yao M, Zhang Q, Liu H, Zheng Z-q, Zhang P, Lin Z, et al. Diesel engine combustion control: medium or heavy EGR. SAE International; 2010.
[45] Yanai T, Han X, Wang M, Reader GT, Zheng M, Tjong J. Clean combustion in a diesel engine using direct injection of neat n-butanol. SAE Int J Engines 2014:1.
[46] Valentino G, Iannuzzi S, Corcione FE. Experimental investigation on the combustion and emissions of a light duty diesel engine fuelled with butanol-diesel blend. SAE International; 2013.
[47] Siwale L, Kristóf L, Adam T, Bereczky A, Mbarawa M, Penninger A, et al. Combustion and emission characteristics of n-butanol/diesel fuel blend in a turbo-charged compression ignition engine. Fuel 2013;107:409–18.
[48] Chen Z, Wu Z, Liu J, Lee C. Combustion and emissions characteristics of high n-butanol/diesel ratio blend in a heavy-duty diesel engine and EGR impact. Energy Convers Manag 2014;78:787–95.
[49] Doğan O. The influence of n-butanol/diesel fuel blends utilization on a small diesel engine performance and emissions. Fuel 2011;90(7):2467–72.
[50] Balamurugan T, Nalini R. Experimental investigation on performance, combustion and emission characteristics of four stroke diesel engine using diesel blended with alcohol as fuel. Energy 2014;78:356–63.
[51] Fushimi K, Kinoshita E, Yoshimoto Y. Effect of butanol isomer on diesel combustion characteristics of butanol/gas oil blend. SAE Technical Paper. 2013.
[52] Valentino G, Corcione FE, Iannuzzi SE, Serra S. Experimental study on performance and emissions of a high speed diesel engine fuelled with n-butanol diesel blends under premixed low temperature combustion. Fuel 2012;92(1):295–307.
[53] Rakopoulos D, Rakopoulos C, Giakoumis E, Dimaratos A, Kyritsis D. Effects of butanol–diesel fuel blends on the performance and emissions of a high-speed DI diesel engine. Energy Convers Manag 2010;51(10):1989–97.
[54] Rakopoulos D, Rakopoulos C, Hountalas D, Kakaras E, Giakoumis E, Papagiannakis R. Investigation of the performance and emissions of bus engine operating on butanol/diesel fuel blends. Fuel 2010;89(10):2781–90.
[55] Merola SS, Tornatore C, Iannuzzi SE, Marchitto L, Valentino G. Combustion process investigation in a high speed diesel engine fuelled with n-butanol diesel blend by conventional methods and optical diagnostics. Renew Energy 2014;64:225–37.
[56] Chen G, Shen Y, Zhang Q, Yao M, Zheng Z, Liu H. Experimental study on combustion and emission characteristics of a diesel engine fueled with 2,5-dimethylfuran–diesel, n-butanol–diesel and gasoline–diesel blends. Energy 2013;54:333–42.
[57] Chen Z, Liu J, Han Z, Du B, Liu Y, Lee C. Study on performance and emissions of a passenger-car diesel engine fueled with butanol–diesel blends. Energy 2013;55:638–46.
[58] Giakoumis EG, Rakopoulos CD, Dimaratos AM, Rakopoulos DC. Exhaust emissions with ethanol or n-butanol diesel fuel blends during transient operation: a review. Renew Sustain Energy Rev 2013;17:170–90.
[59] Karabektas M, Hosoz M. Performance and emission characteristics of a diesel engine using isobutanol–diesel fuel blends. Renew Energy 2009;34(6):1554–9.
[60] Al-Hasan MI, Al-Momany M. The effect of iso-butanol-diesel blends on engine performance. Transport 2008;23(4):306–10.
[61] Ozsezen AN, Turkcan A, Sayin C, Canakci M. Comparison of performance and combustion parameters in a heavy-duty diesel engine fueled with iso-butanol/diesel fuel blends. Energy Explor Exploit 2011;29(5):525–41.
[62] Gu X, Li G, Jiang X, Huang Z, Lee C-f. Experimental study on the performance of and emissions from a low-speed light-duty diesel engine fueled with n-butanol–diesel and isobutanol–diesel blends. Proc Inst Mech Eng Part D J Automob Eng 2013;227(2):261–71.
[63] Chen B, Liu X, Liu H, Wang H, Kyritsis DC, Yao M. Soot reduction effects of the addition of four butanol isomers on partially premixed flames of diesel surrogates. Combust Flame 2017;177:123–36.
[64] Liu H, Li S, Zheng Z, Xu J, Yao M. Effects of n-butanol, 2-butanol, and methyl octynoate addition to diesel fuel on combustion and emissions over a wide range of exhaust gas recirculation (EGR) rates. Appl energy 2013;112:246–56.
[65] Zhang T, Munch K, Denbratt I. An experimental study on the use of butanol or octanol blends in a heavy duty diesel engine. SAE Int J Fuels Lubr 2015;8(3):610–21.
[66] Yao M, Wang H, Zheng Z, Yue Y. Experimental study of n-butanol additive and multi-injection on HD diesel engine performance and emissions. Fuel 2010;89(9):2191–201.
[67] Jeftić M, Tjong J, Reader G, Wang M, Zheng M. Combustion and exhaust gas speciation analysis of diesel and butanol post injection. SAE Int J Engines 2015:1.
[68] Mittal N, Patanwal P, Sithananthan M, Subramanian M, Sehgal AK, Suresh R, et al. Experimental investigation of n-butanol diesel fuel blends on a passenger car. SAE Int J Engines 2015:1.
[69] Zoldy M, Hollo A, Thernesz A. Butanol as a diesel extender option for interna. SAE Int J Engines 2010;1.
[70] Dobre A, Pană C, Nutu N, Negurescu N, Cernat A, Bondoc I. Bio-butanol-alternative fuel for Diesel engine. INMATEH Agricultural Eng 2014;42(1):145–52.
[71] Nigam PS, Singh A. Production of liquid biofuels from renewable resources. Prog Energy Combust Sci 2011;37(1):52–68.
[72] Laza T, Laza Á. Basic fuel properties of rapeseed oil-higher alcohols blends. Fuel 2011;90(2):803–10.
[73] Shadidi B, Yusaf T, Alizadeh HHA, Ghobadian B. Experimental investigation of the tractor engine performance using diesohol fuel. Appl Energy 2014;114:874–9.
[74] Wu H, Nithyanandan K, Zhang J, Lin Y, Lee TH, Lee C, et al. Impacts of acetone–butanol–ethanol (ABE) ratio on spray and combustion characteristics of ABE–diesel blends. Appl Energy 2015;149:367–78.
[75] Jin C, Yao M, Liu H, Lee C-f F, Ji J. Progress in the production and application of n-butanol as a biofuel. Renew Sustain Energy Rev 2011;15(8):4080–106.
[76] Elfasakhany A. Investigations on performance and pollutant emissions of spark-ignition engines fueled with n-butanol–, isobutanol–, ethanol–, methanol–, and acetone–gasoline blends: a comparative study. Renew Sustain Energy Rev 2017;71:404–13.
[77] Bohl T, Tian G, Smallbone A, Roskilly AP. Macroscopic spray characteristics of next-generation bio-derived diesel fuels in comparison to mineral diesel. Appl Energy 2017;186:562–73. Part 3.
[78] Gupta JG, Agarwal AK. Macroscopic and microscopic spray characteristics of diesel and karanja biodiesel blends. SAE International; 2016.
[79] Delacourt E, Desmet B, Besson B. Characterisation of very high pressure diesel sprays using digital imaging techniques. Fuel 2005;84(7–8):859–67.
[80] Heywood JB. Internal combustion engine fundamentals. McGraw-Hill New York; 1988.
[81] Naber JD, Siebers DL. Effects of gas density and vaporization on penetration and dispersion of diesel sprays. SAE technical paper. 1996.
[82] Siebers DL. Liquid-phase fuel penetration in diesel sprays. SAE technical paper. 1998.
[83] Lešnik L, Vajda B, Žunič Z, Škerget L, Kegl B. The influence of biodiesel fuel on injection characteristics, diesel engine performance, and emission formation. Appl energy 2013;111:558–70.
[84] Wloka, J., Potsch, C., and Watchmeister, G. Injection spray visualization for 3000 bar diesel injection. in 24th Conference of the Institute for Liquid Atomization and Spray Systems. 2011.
[85] Wloka JA, Pflaum S, Wachtmeister G. Potential and challenges of a 3000 bar common-rail injection system considering engine behavior and emission level. SAE Int J Engines 2010;3(1):801–13.
[86] Lin Y, Lee T, Nithyanandan K, Zhang J, Li Y, Lee C-F. Experimental investigation and analysis of combustion process in a diesel engine fueled with acetone-butanol-ethanol/diesel blends. SAE International; 2016.
[87] Vasu K, Gupta D, Naeer Siddiquee MW, Nagpal A, Kumar N. Performance and emission characteristics of n-butanol and iso-butanol diesel blend comparison. SAE International; 2015.

5.2 Summary of Article IV

Spray characteristics of n-BA showed some improvement such as further spray penetration and a higher spray volume rate, which resulted in improving spray atomisation, vaporisation and combustion efficiency. The experimental engine test results for the 10n-BA-90 diesel blend showed a slight improvement in BP by 4-5% at medium speed. The highest peak in-cylinder pressure was measured for the iso-BA-diesel blends. Brake-specific fuel consumption (BSFC) and BTE were increased for both iso- and n-BA-diesel blends. CO emissions were reduced with the increase in both n-BA and iso-BA ratios in the diesel blend. CO emissions of iso-BA-diesel blends were lower than that of the equivalent n-BA-diesel blend for most conditions. NO_x emissions and EGT were decreased for both butanol isomers, while n-BA-diesel blends resulted in the lowest emissions for NO_x and UHC. UHC emissions of the n-BA-diesel blend were lower compared to that of iso-BA because the reaction rate is significantly dependent upon the molecular chain structure (the location of the OH group and C-H positions). N-butanol has a straight chain compared to iso-butanol (branched). Therefore, the energy required for cracking the C-H bond is lower, which results in an improved reaction rate and reduced UHC emissions.

The iso-butanol blend has some advantages in relation to in-cylinder pressure, some improvement in brake power and lower CO emissions. Using n-butanol produced better results such as deeper spray penetration with lower EGT, NO_x and UHC emissions. Therefore, because the different isomers of butanol have different beneficial impacts on engine operation, blending n-butanol and iso-butanol together as an additive could yield the individual benefits of each isomer. This is investigated in Chapter 6.

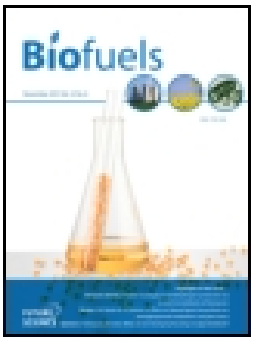
By investigating the effects of n-BA or iso-BA-diesel blends on spray characteristics and engine performance, the BA fermentation industry can be informed about the type of butanol they should produce.

Chapter 6 - Impact of Mixture of n-B and iso-B on Engine Performance

6.1 Article V

Article V: Algayyim, S. J. M., Wandel, A. P., and Yusaf, T., Mixtures of n-butanol and iso-butanol blended with diesel: Experimental investigation of combustion characteristics, engine performance and emission levels in CI engine. *Biofuel,* 2018, pp. 1-10.

Various dual blends of iso-butanol and n-butanol, blended with diesel under various blend ratios, were tested for a range of engine speeds at a compression ratio of 18:1 at full load. All results were compared with neat diesel as a baseline.



Biofuels

ISSN: 1759-7269 (Print) 1759-7277 (Online) Journal homepage: http://www.tandfonline.com/loi/tbfu20

Mixtures of n-butanol and iso-butanol blended with diesel: experimental investigation of combustion characteristics, engine performance and emission levels in a compression ignition engine

Sattar Jabbar Murad Algayyim, Andrew P. Wandel & Talal Yusaf

To cite this article: Sattar Jabbar Murad Algayyim, Andrew P. Wandel & Talal Yusaf (2018): Mixtures of n-butanol and iso-butanol blended with diesel: experimental investigation of combustion characteristics, engine performance and emission levels in a compression ignition engine, Biofuels, DOI: 10.1080/17597269.2018.1493565

To link to this article: https://doi.org/10.1080/17597269.2018.1493565

BIOFUELS
https://doi.org/10.1080/17597269.2018.1493565

Mixtures of n-butanol and iso-butanol blended with diesel: experimental investigation of combustion characteristics, engine performance and emission levels in a compression ignition engine

Sattar Jabbar Murad Algayyim[a,b], Andrew P. Wandel[a] and Talal Yusaf[a]

[a]School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, Queensland, Australia; [b]Department of Mechanical, College of Engineering, University of Al-Qadisiyah, Al-Diwaniyah, Iraq

ABSTRACT

The isomers of butanol have slightly different properties, which can be exploited to improve combustion characteristics. To investigate the potential of this concept, normal-butanol (nB) and iso-butanol (isoB) were blended together in four different ratios (5% of each, 10% of each, and 7% plus 13% of each in both variations, by volume) with conventional diesel. The experimental data were analyzed via analysis of variance to evaluate significant differences between engine parameters. Brake power for the 5% isoB–5% normal-butanol–90% diesel blend was slightly improved while specific fuel consumption was increased with the increase in all dual blends. The high blend ratios of isoB (10% and 13% isoB) produced higher peak in-cylinder pressures and heat release rates as well as a substantial reduction in carbon monoxide emissions. The higher blend ratios of nB (10% and 13% nB) produced much lower unburnt hydrocarbon emissions because the energy required to crack the C–H bonds of nB is less than that required for isoB. Therefore, the hydrocarbons are more easily oxygenated. A slight reduction was found in NO_x emissions when increasing either nB or isoB, with nB being slightly more effective. Therefore, a blend of n- and isoB could be a promising alternative to a single isomer additive (iso/nB) to optimize engine performance.

ARTICLE HISTORY
Received 7 March 2018
Accepted 17 May 2018

KEYWORDS
Iso-butanol; n-butanol

Nomenclature

θ	crank angle
γ	ratio of specific heats
5isoB-5nB -90D	5%iso-butanol-5%normal-butanol-90% diesel
7isoB-13nB-80D	7%iso-butanol-13%normal-butanol-80% diesel
10isoB-10nB -80D	10%iso-butanol-10%normal-butanol-80% diesel
13isoB-7nB-80D	13%iso-butanol-7%normal-butanol-80% diesel
CA	crank angle
CO	carbon monoxide
CO_2	carbon dioxide
D100	diesel 100
DI	direct injection
EGR	exhaust gas recirculation
EGT	exhaust gas temperature
HRR	heat release rate
isoB	iso-butanol
nB or 1B	normal-butanol
NO_x	nitrogen oxides
PM	particular matter
rpm	revolutions per minute
secB	sec-butanol
SFC	specific fuel consumption
T	torque
tertB	tert-butanol
UHC	unburnt hydrocarbon

Introduction

The limited fossil fuels reserves together with a growing energy demand in the world have accelerated research into renewable, sustainable and environmentally friendly energy resources such as alcohols to reduce engine emission levels and the dependence on conventional fuel [1,2]. The utilization of alcohols as an additive blend into diesel fuel is increasing because of their beneficial properties [3–6] such as their ability to be produced from renewable sources such as waste crops [7–11], high oxygen content which could enhance combustion efficiency, high heat of vaporization, and peak combustion temperature reduction, consequently leading to NO_x emissions reduction and engine power improvement [7,8,12]. Long-chain alcohols (such as butanol) are suitable additives to diesel fuel compared to ethanol due to their reduced corrosive impact on fuel injection systems, higher flash point making them safer for storage and distribution, and higher energy content [13]. There are four different isomers of butanol: normal or 1 butanol (nB), iso-butanol (isoB), sec-butanol (secB) and tert-butanol (tertB).

Exhaust gas emission levels are reduced as a result of the addition of butanol blends because they have substantial oxygen content and correspondingly lower hydrocarbon content than gasoline or diesel. IsoB and nB as additive blends to conventional diesel have been extensively investigated under different blend ratios and operating conditions because the fermentation of isoB and nB is strongly established in the bio butanol production sector compared to that of sec- or tert-butanol. Some previous studies have investigated the effect on characteristic engine performance by using isoB or nB as a single fuel or as an additive [14–20]. Zheng et al. [21] investigated the four butanol isomers in a compression ignition (CI) engine. The higher heat release was retarded as a result of adding butanol to diesel blends. A summary of previous studies is presented below. It has been found that nB ignition delay time is shorter than

---

CONTACT Sattar Jabbar Murad Algayyim ✉ Sattarjabbarmurad.algayyim@usq.edu.au; ialiraq12@yahoo.com School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, Queensland 4350, Australia

that of isoB, and the peak in-cylinder pressure was higher as a consequence of the increased ignition delay time [22–25]. However, the burning velocity of isoB is higher because of the different positions of the C–H bonds [23]. Both isomers reduce carbon monoxide (CO) emissions [26]. The isoB isomer decreases NO_x emissions [24,25], but increases unburned hydrocarbon (UHC) emissions [23]. The behavior of nB is the opposite: NO_x emissions were found to increase [24,25], but UHC emissions decreased [23]. The action of exhaust gas recirculation (EGR) reverses the NO_x and UHC emissions behavior of nB, while isoB maintains the same trend [16]. Soot formation of isoB was lower than that for nB [27]. EGR reduces smoke opacity [16].

Because the different isomers of butanol have different beneficial effects on engine operation, blending them together as an additive could yield the overall individual benefits of each isomer.

The aim of this study is to evaluate and analyze the effect of using a dual blend of isoB and nB with neat diesel in a CI engine by studying the performance of the diesel engine.

Experimental setup

Fuel preparation and properties

The butanol isomers investigated in this study (nB, $CH_3CH_2CH_2CH_2OH$ and isoB, $(CH_3)_2CH_2CHOH$) were 99.8% analytical grade. The isoB and nB blend was mixed with four ratios by volume and blended with neat diesel (Table 1). ASTM 1298 was followed to measure the blends' density. The dynamic viscosities of the test fuel were measured at 40 °C by using a Brookfield Viscometer and then the kinematic viscosities were calculated. A digital oxygen bomb calorimeter (XRY-1A) following ASTM D240 was used to measure the blends' heating values. The fuel blends' properties are presented in Figure 1.

Engine test setup

The engine test was conducted using a CT 300 variable compression diesel engine. Direct injection was used with a mechanical injector with three holes with an injection pressure of 300 bar. The specifications of the diesel engine used in this study are listed in Table 2. The engine load was controlled using an electric dynamometer connected to the engine. A Kistler pressure transducer connected to the data collection system was used to measure the in-cylinder pressure. A thermocouple inserted on the exhaust system was used to measure exhaust gas temperature (EGT). Figure 2 shows a schematic of the test setup. A Coda gas analyzer was used to measure exhaust gas emission levels (NO_x, UHC, and CO). The accuracy ranges of the engine equipment and the gas analyzers are listed in Table 3.

Table 1. Fuel blend ratios by volume.

Blend	iso-butanol (isoB)	n-butanol (nB)	Diesel (D)
D			100%
5isoB-5nB-90D	5%	5%	90%
7isoB-13nB-80D	7%	13%	80%
10isoB-10nB-80D	10%	10%	80%
13isoB-7nB-80D	13%	7%	80%

Engine test conditions

For each blend test, the engine was operated for at least 20 minutes before recording commenced. Density and heating value were included in each engine run to account for the amount of fuel injected. For accurate measurement results, the engine performance (including in-cylinder pressure, brake power (BP), BSFC, and EGT) and the emission data (including NO_x, UHC, and CO) were repeated at least three times before being recorded. Error bars show the range of measurements.

The heat release rate was calculated according to Eq. (1) [28] and this calculation of the heat release rate is carried out without including the wall heat losses, where Q is the heat release, θ is the crank angle, P is the in-cylinder pressure, γ is the ratio of specific heats equal to 1.35 [4]:

$$\begin{aligned}\frac{dQ_n}{d\theta} &= \frac{\gamma}{\gamma-1}\ P\frac{dV}{d\theta} + \frac{1}{\gamma-1}\ V\frac{dP}{d\theta}\\ &= \left(\frac{\gamma}{\gamma-1} \times\ P_I \times (V_{i+1} - V_i) + \frac{1}{\gamma-1} \times V_I\ \times (P_{i+1} - P_i)\right)/\Delta\theta\end{aligned} \tag{1}$$

Brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE) are calculated according to the following equations [29]:

$$\mathrm{BSFC} = \frac{\mathrm{SFC}\ \times\ 10^6}{\mathrm{BP}} \tag{2}$$

Table 2. Engine specifications.

Engine model	CT 300, GUNT Hamburg
Combustion type	Direct Injection Engine
Number of cylinders	1
Speed range (rpm)	900–3000
Bore	90 mm
Stroke	74 mm
Connecting rod	128
Maximum compression pressure	60–80 bar
Nozzle injection pressure	300 bar
Nozzle diameter (mm)	0.18
Exhaust closes	4.5 … 6.7° ATDC
Inlet opens	5.2 … 7.5° BTDC
Engine speeds test @ full load	1400, 2000 & 2600 RPM
Compression ratio test	18:1

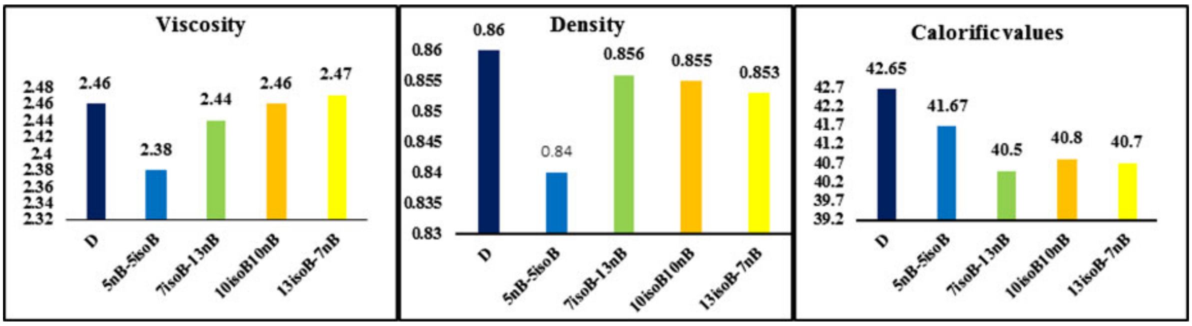


Figure 1. Measured properties of test blends.

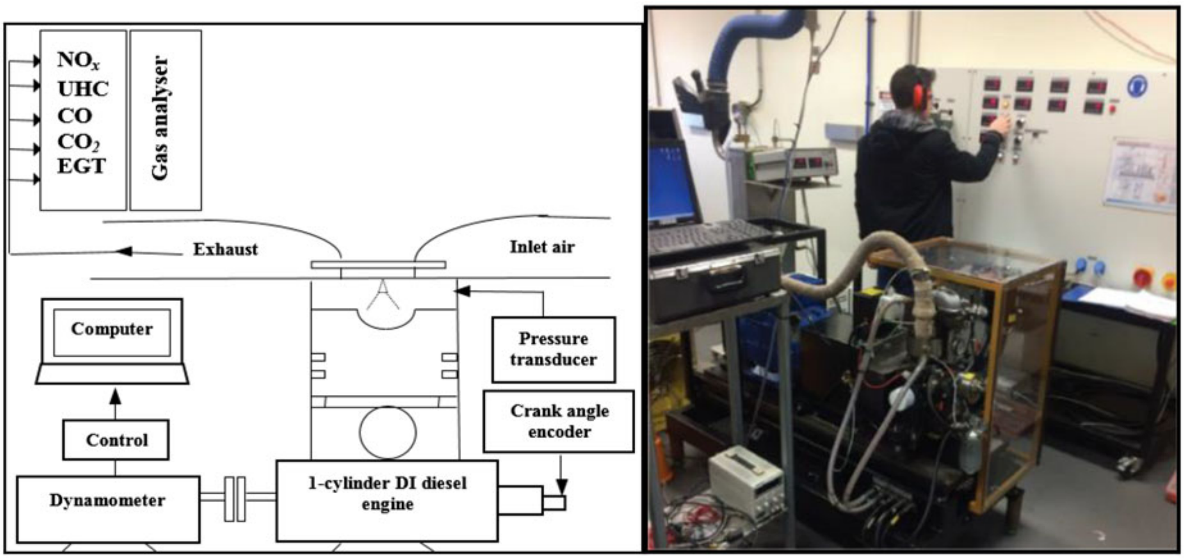


Figure 2. Schematic diagram of engine test setup.

Table 3. Measurement equipment resolution.

Parameter	Source	Resolution	Accuracy (±)
In-cylinder pressure	Pressure transducer in cylinder head	0.01 bar	1%
Fuel flow	Mass flow rate	0.001 L/h	0.1%
Speed	Tachometer on output shaft	0.0001 rpm	0.0%
Exhaust gas temperature	Thermocouple in exhaust system	0.001 °C	1 °C
Torque	Load dynamometer	0.001 Nm	1%
Exhaust gas composition	NO_x	10 ppm	0.1%
	CO	0.01%	0.01%
	UHC	10 ppm	0.01%

$$\mathrm{BTE} = \frac{3600}{\mathrm{BSFC} \ \times \ \mathrm{calrorific\ value}} \times 100 \tag{3}$$

where SFC is the fuel mass flow rate (accounting for the amount of fuel injected depending on density of each fuel blend at each engine test).

Statistical analysis

The experimental data of the engine test was analyzed using the SPSS statistics 24 software package. One-way analysis of variance (ANOVA) and Bonferroni post-hoc tests were conducted to study the significance of the impact of independent variables of dual fuel blends type on the dependent variables BP, SFC, NO_x, CO, and UHC [30]. The results of these tests are included in Tables 4 and 5.

Engine test results and discussion

Combustion characteristics

In-cylinder pressure

Figures 3 and 4 show the in-cylinder pressure trace for the test fuels at the two tested engine speeds. The ignition time for all the nB–isoB mixtures was delayed by approximately the same amount compared to neat diesel due to the lower cetane number (CN) of both butanol isomers. At the lowest engine speed, increasing the overall butanol content decreased the peak pressure. However, at the higher engine speeds, the reverse occurred: higher levels of isoB tended to increase the peak pressure. This is a result of the lower CN of butanol increasing the ignition delay time, allowing for better fuel-air mixing, which produces very rapid burning rates and consequential high peak pressures [14,24,31]. The nB ignition delay period is shorter than that of isoB [22], and hence the variation between the blends.

Table 4. One-way ANOVA test of engine performance and emissions and their statistical significance.

Source	Dependent variable	Degrees of freedom	Mean Square	F	Sig.
Fuel	BP	4	0.09	0.07	1
	SFC	4	0.143	0.01	0.998
	EGT	4	170.35	0.049	0.994
	NO_x	4	176.924	0.031	0.996
	CO	4	0.180	2.182	0.145
	UHC	4	5280.781	52.548	0

Figure 5 shows the standard deviation of the maximum pressure observed for the dual test blends. It can be recognized that the variability increases with increasing amounts of isoB, although the maximum standard deviation is less than 1% of the average. Standard deviation values were increased at 2000 rpm engine speed because combustion was less stable as a consequence of reduced time to complete the reaction.

Heat release rate

Figures 6 and 7 also show the heat release rate (HRR) of the test fuels at the two tested engine speeds. All alcohol dual blends showed high HRR at 2000 rpm engine speed compared to neat diesel. The high blend ratios of isoB (10% and 13% isoB) produced higher HRR at 1400 and 2000 rpm compared to 5% and 13% nB because isoB has a lower CN compared to nB (15 vs 25) [4]. The low CN and boiling point of both butanol isomers produced a more combustible mixture during the ignition delay period. Moreover, the higher laminar flame speed of isoB leads to a higher heat release rate [23]. Larger chain alcohols such as butanol

Table 5. Descriptive statistics summary for performance parameters.

	D		5isoB-5onB-90D		7isoB-13nB-80D		10isoB-10onB-80D		13isoB-7nB-80D	
Dependent variable	M	SD	M	SD	M	SD	M	SD	M	SD
BP (kW)	3.95a	1.07	3.96a	1.09	3.91a	1.11	3.83a	1.09	3.91a	1.08
SFC (kg/h)	1.263a	0.361	1.309a	0.358	1.3a	0.396	1.302a	0.395	1.311a	0.378
EGT (°C)	491.7a	57.4	482a	58	474a	62.6	473.7a	58	477a	58.9
NO_x (ppm)	789.22a	76.99	766.11a	76.11	769.44a	77.1	774.5a	76.9	784a	73
CO (%)	1.251a	0.459	0.81b	0.24	0.688b	0.195	0.733b	0.237	0.64b	0.22
UHC (ppm)	195.66a	11.9	178.2a	4.7	107.83ab	5.83	100.44b	15.95	146.77c	6.98

Means in the same row that do not share the same letter are significantly different.

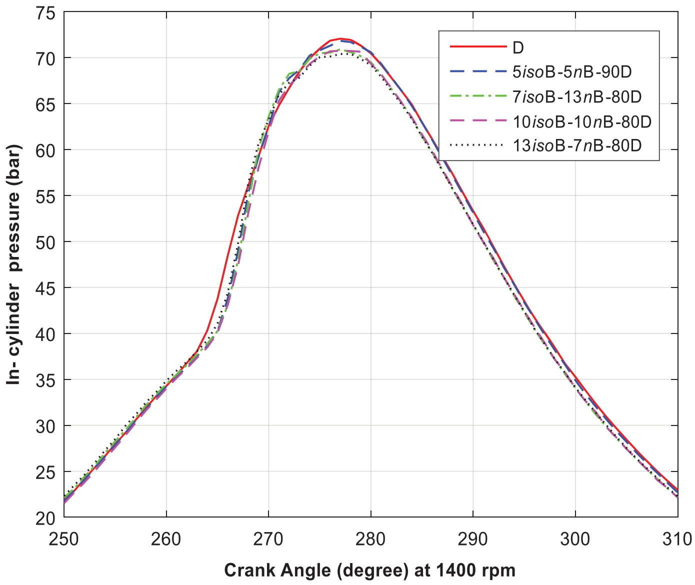


Figure 3. In-cylinder pressure of test blends at engine speed 1400 rpm. Top dead center (TDC) is shown at 270° crank angle.

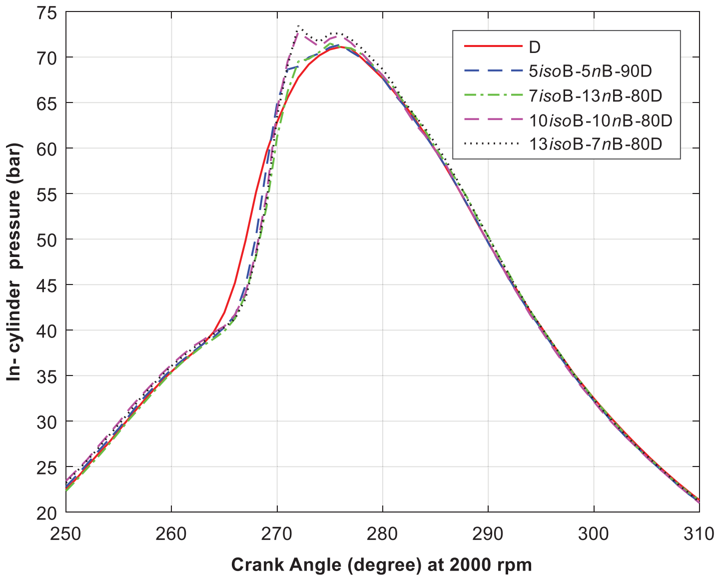


Figure 4. In-cylinder pressure of test blends at engine speed 2000 rpm. TDC is shown at 270° crank angle.

have a higher flame speed (45 cm/s) than neat diesel (33 cm/s) [32,33], so will create a higher heat release rate.

Engine performance and emissions characteristics

The ANOVA summary of engine test results is given in Table 4, with the only significant differences obtained for UHC and CO emissions. The descriptive statistics results and the Bonferroni test are presented in Table 5 to study the differences between the independent variables. This data informs the discussion below.

BP, BSFC, and BTE

BP and torque (T) were marginally reduced for most dual alcohol-diesel blends (Figures 8 and 9). All dual alcohol-diesel blends showed an increase in BSFC (Figure 10) because of the smaller additives' heating values, as expected [16]. However, this increment in BSFC is also not significant

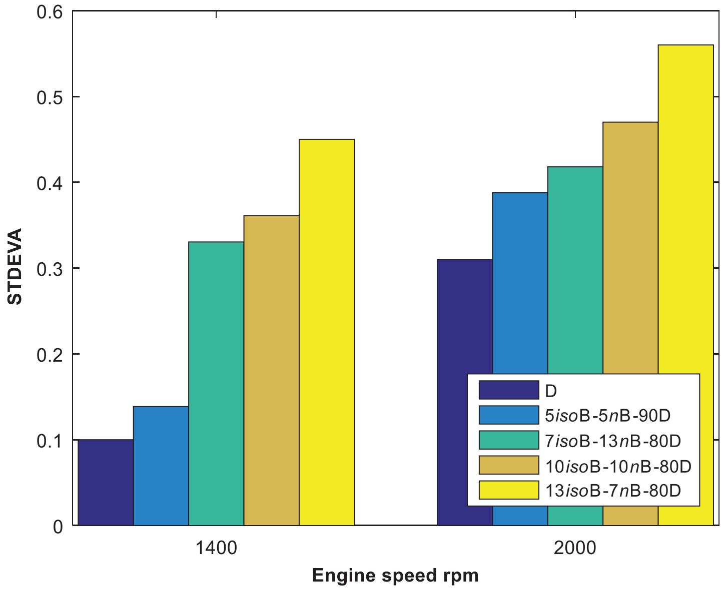


Figure 5. Standard deviation of the maximum pressure observed of test blends at two engine speeds.

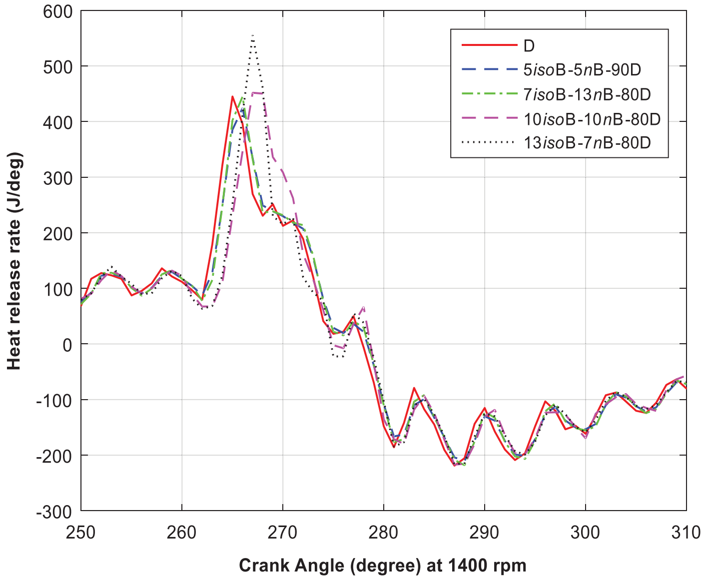


Figure 6. Heat release rate of test blends at engine speed 1400 rpm.

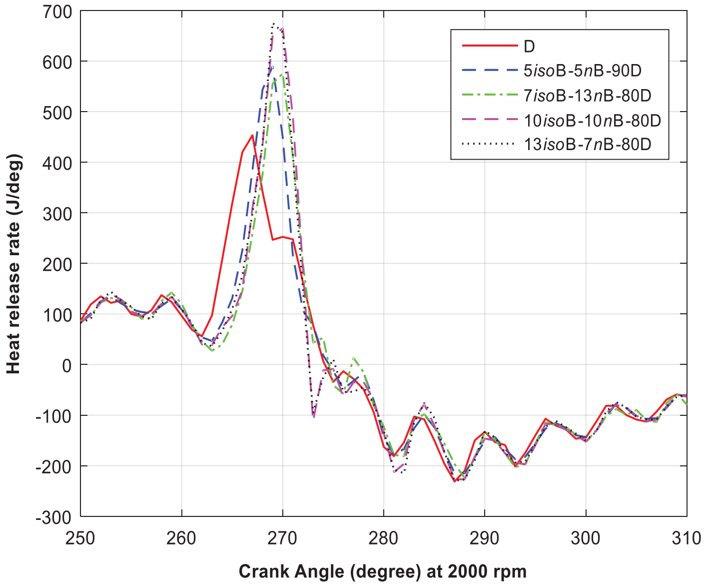


Figure 7. Heat release rate of test blends at engine speed 2000 rpm.

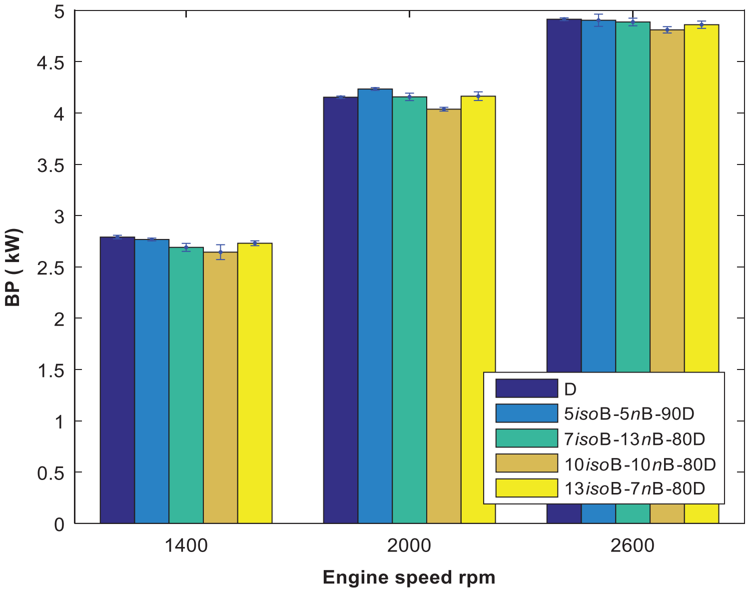


Figure 8. BP of test fuels.

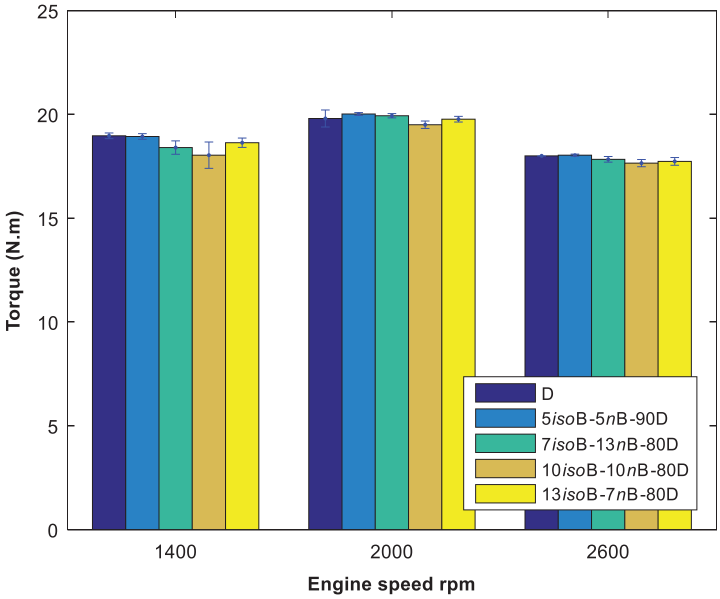


Figure 9. T of test fuels.

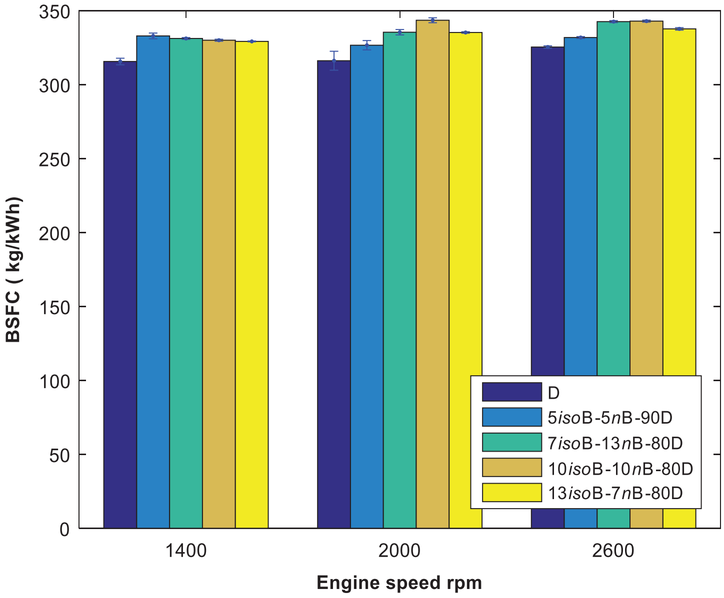


Figure 10. BSFC of test fuels.

(Table 5). All dual blends have higher combustion efficiency because of their high oxygen content, which results in improving the combustion rate when using as an additive blend. Rakopoulos et al. [18] reported that BTE was increased as a result of adding butanol to diesel blend because butanol-diesel fuel blends have a lower cetane number than diesel, which causes a longer ignition delay. Consequently, there is a wider range in the fraction of fuel burned in the premixed mode, which elevates BTE (Figure 11). As the isoB blend rate increases, the BTE increases due to the low CN number.

EGT and NO$_x$ formation

EGT was reduced as a result of the added isoB and nB (Figure 12), due to the higher latent heat of vaporization and the lower energy content of both butanol isomers. This reduction is not significant (Table 5). Because NO$_x$ emissions are highly sensitive to temperature, there is a corresponding slight decrease in NO$_x$ emissions (Figure 13), but this is also an insignificant difference.

CO and UHC

The presence of butanol significantly decreased the CO emissions (Figure 14), due to the oxygen in the fuel encouraging complete combustion. Increasing the amount of isoB possibly reduces the CO emissions more effectively than nB, but these results are not conclusive (Table 5).

Increasing the amount of butanol in the dual alcohol blends significantly reduces UHC emissions (Figure 15), with nB being significantly more effective than isoB (Table 5). Because the energy needed to crack the C–H bonds of nB is less than for isoB, the hydrocarbons are more easily oxygenated [22,23].

Moreover, adding butanol significantly reduces UHC emissions by enhancing the evaporation speed of the droplet due to butanol's low boiling point and viscosity. This

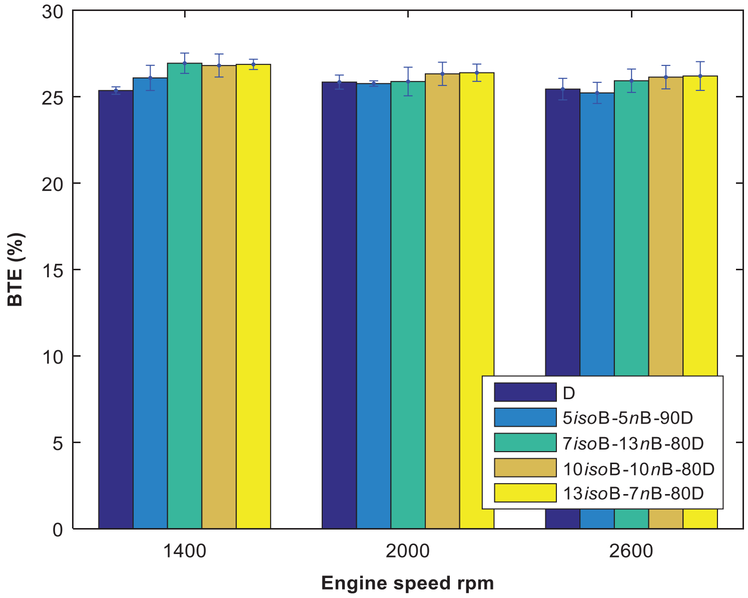


Figure 11. BTE of test fuels.

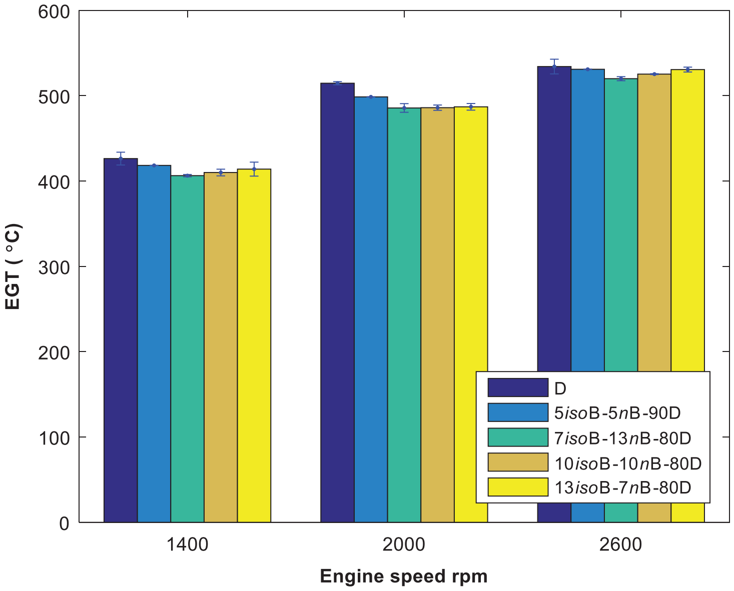


Figure 12. EGT of test fuels.

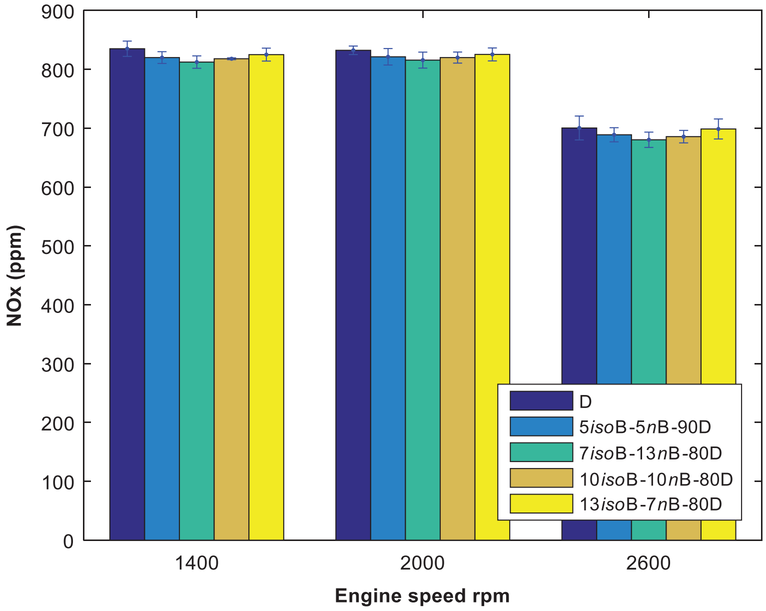


Figure 13. NO_x emissions of test fuels.

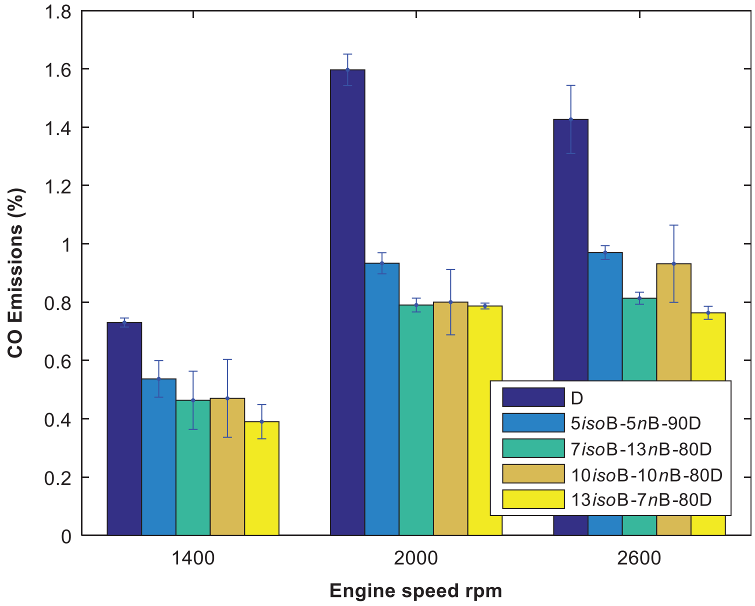


Figure 14. CO emissions of test fuels.

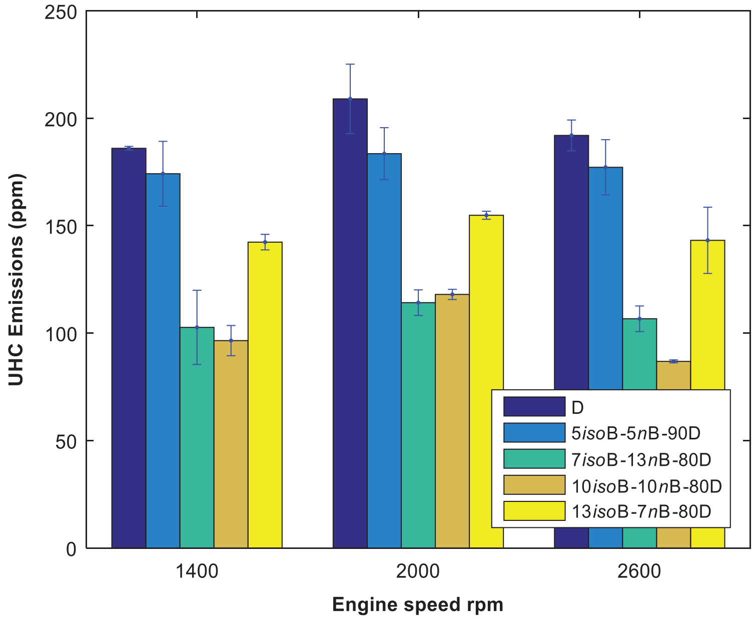


Figure 15. UHC emissions of test fuels.

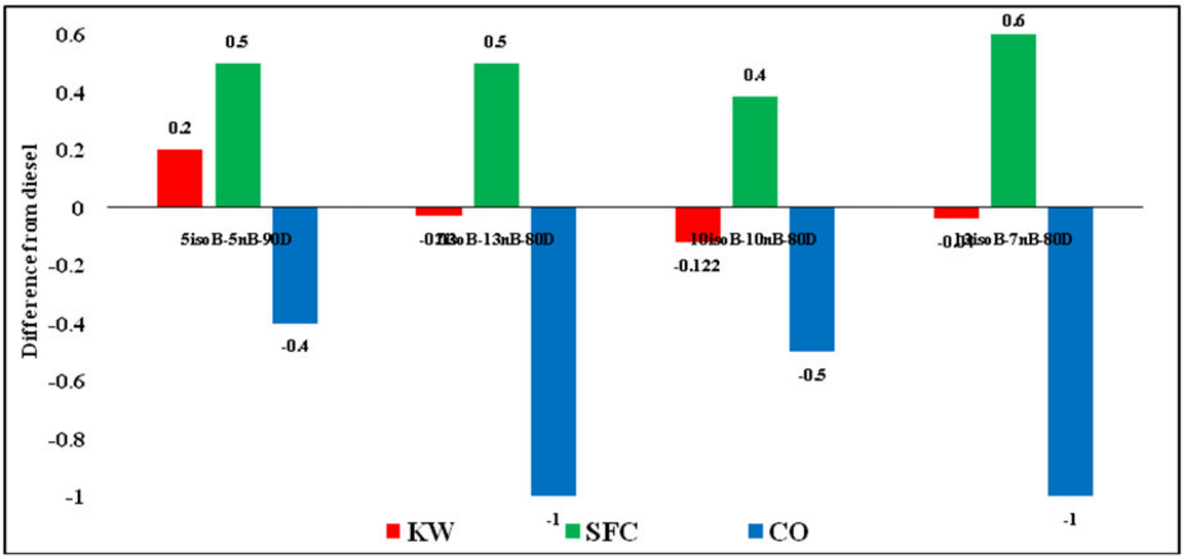


Figure 16. Comparison of differences between BP, BSFC, and CO of different dual blends of isoB and nB with diesel blends and neat diesel averaged over three engine speeds.

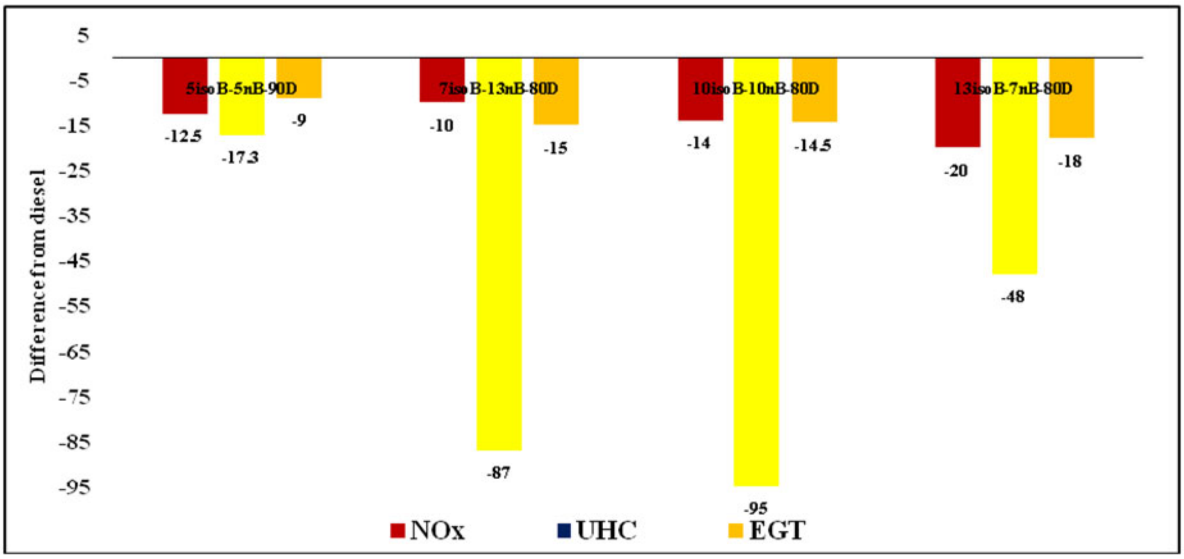


Figure 17. Comparison of differences of emission levels (NO_x, UHC, and EGT) of different dual fuel blends of isoB and nB with diesel blends and neat diesel averaged over three engine speeds.

therefore reduced the diameter size and lifetime of the droplet. Droplet clouds have a significant impact on turbulent flame propagation, which enhances the combustion rate. Therefore, the degree of pre-evaporation and the size of the droplet are important factors to control the burning velocity [34]. Therefore, the low boiling points of butanol isomers can enhance the evaporation rate, which encourages mixing, thereby improving the combustion rate.

Figure 16 shows a comparison of the differences between BP, SFC, and CO of different dual fuel blends of isoB and nB with diesel blend and neat diesel averaged over three engine speeds. Figure 17 summarizes the comparison of the differences between NO_x, UHC, and EGT of different dual fuel blends of isoB and nB with diesel blend and neat diesel averaged over three engine speeds.

Conclusion

The experiments studied here revealed the behavior of the test fuel blends relating to engine performance. The BP of the 5% isoB–5% normal-butanol–90% blend was slightly improved while the BSFC was increased with the increase in all dual blends. The 13% isoB in the dual fuel blend produced the maximum in-cylinder pressure and resulted in the highest HRR. Including dual alcohol significantly reduced CO emissions due to the oxygenation of the fuel supporting conversion to CO_2; isoB appears to be slightly more effective at reducing CO emissions than nB. While both isomers significantly reduced UHC emissions, nB was significantly more effective because of its favorable chemical structure. A slight reduction was found in NO_x emissions with an increase in both isoB and nB because the heat of vaporization of both isoB and nB were higher. NO_x formation is also a slow chemical reaction, so the increased ignition delay and corresponding reduced combustion time limit the potential for forming NO_x.

In conclusion, the 10% dual fuel blend produced some improvement in BP and comparable values of in-cylinder pressure. The higher ratio of isoB possibly produced the best CO reduction while the high ratio of nB blend produced the best overall reduction in UHC and NO_x.

Acknowledgments

The first author thanks the Iraqi Government Ministry of Higher Education and Scientific Research for supporting the research. The authors are also grateful to Mr. Brian Lenske for his assistance with the experiments and Dr. Rachel King for her assistance with the statistical analysis.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1] Shuai C, Shen L, Jiao L, et al. Identifying key impact factors on carbon emission: Evidences from panel and time-series data of 125 countries from 1990 to 2011. Appl Energ. 2017;187:310–325.

[2] Gupta RB, Demirbas A. Gasoline, diesel, and ethanol biofuels from grasses and plants. New York: Cambridge University Press; 2010.

[3] Algayyim SJM, Wandel AP, Yusaf T, et al. Production and application of ABE as a biofuel. Renew Sustain Energ Rev. 2018:82(Part 1):1195–1214.

[4] Algayyim SJM, Wandel, AP, Yusaf T, et al. The impact of n-butanol and iso-butanol as components of butanol-acetone (BA) mixture-diesel blend on spray, combustion characteristics, engine performance and emission in direct injection diesel engine. Energy. 2017;140(Part 1):1074–1086.

[5] Algayyim SJM, Wandel AP, Yusaf T, et al. Impact of butanol-acetone mixture as a fuel additive on diesel engine performance and emissions. Fuel. 2018;227:118–126.

[6] Algayyim SJM, Wandel AP, Yusaf T. Experimental and numerical investigation of spray characteristics of butanol-diesel blends. In 11th Asia-Pacific Conference on Combustion; 2017 Dec 10–14. NSW Australia: The University of Sydney.

[7] Algayyim SJM, Wandel AP, Yusaf T, et al. The experimental investigation of butanol-diesel blend on engine performance and emission levels in DI diesel engine. In ISCA. 2017 Dec 5–6. Melbourne, Australia: Swinburne University.

[8] Algayyim SJM, Wandel AP, Yusaf T, et al. Experimental study of spray characteristics, engine performance and emission levels of acetone-butanol-ethanol mixture-diesel blends in a diesel engine. In 11th Asia-Pacific Conference on Combustion; 2017 Dec 10–14. NSW, Australia: The University of Sydney.

[9] Algayyim SJM, Wandel AP, Yusaf T. The effect of butanol-acetone mixture-cottonseed biodiesel blend on spray characteristics, engine performance and emissions in diesel engine. In 11th Asia-Pacific Conference on Combustion; 2017 Dec 10–14. NSW, Australia: The University of Sydney.

[10] Trindade WRS, dos Santos RG. Review on the characteristics of butanol, its production and use as fuel in internal combustion engines. Renew Sustain Energ Rev. 2017;69:642–651.

[11] Kandasamy M, Hamawand I, Bowtell L, et al. Investigation of ethanol production potential from lignocellulosic material without enzymatic hydrolysis using the ultrasound technique. Energies. 2017;10(1):62.

[12] Elfasakhany A. Investigations on performance and pollutant emissions of spark-ignition engines fueled with n-butanol–, isobutanol–, ethanol–, methanol–, and acetone–gasoline blends: A comparative study. Renew Sustain Energ Rev. 2017;71:404–413.

[13] Liu H, Hu B, Jin C. Effects of different alcohols additives on solubility of hydrous ethanol/diesel fuel blends. Fuel. 2016;184:440–448.

[14] Siwale L, Kristóf L, Adam T, et al. Combustion and emission characteristics of n-butanol/diesel fuel blend in a turbo-charged compression ignition engine. Fuel. 2013;107:409–418.

[15] Altum S, Öner C, Yaşar, F, et al. Effect of n-butanol blending with a blend of diesel and biodiesel on performance and exhaust emissions of a diesel engine. Ind Eng Chem Res. 2011;50(15):9425–9430.

[16] Vasu K, Gupta D, Naseer Siddiquee, et al. Performance and emission characteristics of n-butanol and Iso-butanol diesel blend comparison. Warrendale, USA:SAE International; 2015.

[17] Saravanan S, Rajesh Kumar B, Varadharajan A, et al. Optimization of DI diesel engine parameters fueled with iso-butanol/diesel blends – Response surface methodology approach. Fuel. 2017;203(Supplement C):658–670.

[18] Rakopoulos D, Rakopoulos C, Hountalas D, et al. Investigation of the performance and emissions of bus engine operating on butanol/diesel fuel blends. Fuel. 2010;89(10):2781–2790.

[19] Dobre A, Pană C, Nuīu, N, et al. Bio-butanol-alternative fuel for Diesel engine. INMATEH Agric Eng. 2014;42(1):145–152.

[20] Chen Z, Wu Z, Liu J, et al. Combustion and emissions characteristics of high n-butanol/diesel ratio blend in a heavy-duty diesel engine and EGR impact. Energy Convers Manag. 2014;78:787–795.

[21] Zheng Z, Li C, Liu H, et al. Experimental study on diesel conventional and low temperature combustion by fueling four isomers of butanol. Fuel. 2015;141:109–119.

[22] Pan L, Zhang Y, Tian Z, et al. Experimental and kinetic study on ignition delay times of Iso-butanol. Energy Fuels. 2014;28(3):2160–2169.

[23] Wu F, Law CK. An experimental and mechanistic study on the laminar flame speed, Markstein length and flame chemistry of the butanol isomers. Combust Flame. 2013;160(12):2744–2756.

[24] Gu X, Li G, Jiang X, et al. Experimental study on the performance of and emissions from a low-speed light-duty diesel engine fueled with n-butanol–diesel and isobutanol–diesel blends. Proc Inst Mech Eng D. 2013;227(2):261–271.

[25] Ozsezen AN, Turkcan A, Sayin C, et al. Comparison of performance and combustion parameters in a heavy-duty diesel engine fueled with Iso-butanol/diesel fuel blends. Energy Explor Exploit. 2011;29(5):525–541.

[26] Zhang T, Munch K, Denbratt I. An experimental study on the use of butanol or octanol blends in a heavy duty diesel engine. SAE Int J Fuels Lubr. 2015;8(3):610–621.

[27] Chen B, Liu X, Liu H, et al. Soot reduction effects of the addition of four butanol isomers on partially premixed flames of diesel surrogates. Combust Flame. 2017;177:123–136.

[28] Heywood JB. Internal combustion engine fundamentals. New York: McGraw-Hill; 1988.

[29] Emiroğlu AO, Şen M. Combustion, performance and emission characteristics of various alcohol blends in a single cylinder diesel engine. Fuel. 2018;212:34–40.

[30] Al-Lwayzy SH, Yusaf, T. Diesel engine performance and exhaust gas emissions using Microalgae Chlorella protothcoides biodiesel. Renew Energy. 2017;101:690–701.

[31] Jeftić M, Tjong J, Reader G, et al. Combustion and exhaust gas speciation analysis of diesel and butanol post injection. SAE Int J Fuels Lubr. 2015;1:803–816.

[32] Veloo PS, Egolfopoulos FN. Flame propagation of butanol isomers/air mixtures. Proc Combust Inst. 2011;33(1):987–993.

[33] Sarathy SM, Thomson MJ, Togbé C, et al. An experimental and kinetic modeling study of n-butanol combustion. Combust Flame. 2009;156(4):852–864.

[34] Wandel AP, Chakraborty N, Mastorakos E. Direct numerical simulations of turbulent flame expansion in fine sprays. Proc Combust Inst. 2009;32(2):2283–2290.

6.2 Summary of Article V

Engine performance and emissions of diesel engines were tested and evaluated using a dual blend of n-B and iso-B. Normal-butanol and isoB blends were blended together in four different ratios (5% of each, 10% of each, and 7% plus 13% of each in both variations, by volume) with conventional diesel. The experimental data were statistically assessed using ANOVA to evaluate whether variations in parameters due to the different fuels were significant.

Using a dual blend with 10% of each produces a slight improvement in BP. The highest ratio of iso-butanol in the dual blend showed the maximum in-cylinder pressure and much lower CO emissions, while a high ratio of n-butanol in the dual blend produced lower NO_x emissions. High ratios of either iso- or n-butanol in dual blends produced UHC emissions reductions. Therefore, a blend of n- and iso-B could be a promising alternative to a single isomer additive (iso/n-B) to optimise engine performance. This should be investigated for further operating conditions and blend ratios.

Chapters 4 and 5 show that using a BA blend as an additive to conventional diesel in CI engines is beneficial due to improved spray characteristics and the chemical properties of BA, which improve performance while reducing emissions. This is expanded upon in **Chapter 7**, which investigates and evaluates the impact of adding BA to cottonseed biodiesel on spray characterises and engine performance, with the intention of normalising the fluid properties of biodiesel towards conventional diesel and also mitigating the increased NO_x emissions observed from biodiesels.

Chapter 7 - Impact of BA-Biodiesel on Spray and Engine Performance

7.1 Article VI

Algayyim, S. J. M., Wandel, A. P., Yusaf, T., and Al-Lwayzy, S., Butanol-Acetone Mixture Blended with Cottonseed Biodiesel: Spray Characteristics Evolution, Combustion Characteristics, Engine Performance and Emission. *Proceedings of the Combustion Institute*, 2018. 37: pp. 1-11.

This chapter investigates spray characteristics and engine performance using BA blended with cottonseed biodiesel for various blend ratios. Spray tests were carried out in a CVV for different injection conditions. A high-speed camera was used to record spray images and macroscopic spray characteristics (spray penetration, spray cone angle and spray volume) were measured. Engine tests were conducted using a single-cylinder DI diesel engine at three engine speeds (1400, 2000 and 2600 rpm) and a compression ratio of 18:1 at full load. The engine's performance was evaluated using in-cylinder pressure, BP, BSFC, BTE, EGT and HRR. Emission characteristics (NO_x, UHC, CO and CO_2) were also measured and analysed. The experimental data were statistically assessed using ANOVA to evaluate whether variations in parameters due to the different fuels were significant.

Available online at www.sciencedirect.com

ScienceDirect

Proceedings of the Combustion Institute 37 (2019) 4729–4739

Proceedings of the Combustion Institute

www.elsevier.com/locate/proci

Butanol–acetone mixture blended with cottonseed biodiesel: Spray characteristics evolution, combustion characteristics, engine performance and emission

Sattar Jabbar Murad Algayyim [a,b,*], Andrew P. Wandel [a], Talal Yusaf [a,c], Saddam Al-Lwayzy [a]

[a] *School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, QLD 4350, Australia*
[b] *Department of Mechanical, College of Engineering, University of Al-Qadisiyah, Al-Diwaniyah, Iraq*
[c] *Pro Vice Chancellor VC Federation University Australia, Ballarat VIC, Australia*

Received 30 November 2017; accepted 23 August 2018
Available online 6 September 2018

Abstract

Increasing energy demands and more stringent legislation relating to pollutants such as nitrogen oxide (NO_x) and carbon monoxide (CO) from fossil fuels have accelerated the use of biofuels such as biodiesel. However, current limitations of using biodiesel as an alternative fuel for CI engines include a higher viscosity and higher NO_x emissions. This is a major issue that could be improved by blending biodiesel with alcohols. This paper investigates the effect of a butanol–acetone mixture (BA) as an additive blended with biodiesel to improve the latter's properties. Macroscopic spray characteristics (spray penetration, spray cone angle and spray volume) were measured in constant volume vessel (CVV) at two injection pressures. A high-speed camera was used to record spray images. The spray's edge was determined using an automatic threshold calculation algorithm to locate the spray outline (edge) from the binary images. In addition, an engine test was carried out experimentally on a single-cylinder diesel engine. The engine's performance was measured using in-cylinder pressure, brake power (BP) and specific fuel consumption (SFC). Emission characteristics NO_x, CO and UHC were also measured. Neat biodiesel and three blends of biodiesel with up to 30% added BA were tested. The experimental data were analyzed via ANOVA to evaluate whether variations in parameters due to the different fuels were significant. The results showed that BA can enhance the spray characteristics of biodiesel by increasing both the spray penetration length and the contact surface area, thereby improving air–fuel mixing. The peak in-cylinder pressure for 30% BA was comparable to neat diesel and higher than that of neat biodiesel. Brake power (BP) was slightly improved for 10% BA at an engine speed of 2000 rpm while SFC was not significantly higher for any of the BA-biodiesel blends because of the smaller heating

---

[*] Correspondence author at: School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, QLD 4350, Australia.

E-mail addresses: Sattarjabbarmurad.algayyim@usq.edu.au, ialiraq12@yahoo.com (S.J.M. Algayyim).

https://doi.org/10.1016/j.proci.2018.08.035

value of BA. Comparing the effect on emissions of adding BA to biodiesel, increasing the amount of BA reduced NO_x and CO (7%) and (40%) respectively compared to neat biodiesel, but increased UHC.

Keywords: Butanol–acetone mixture; Biodiesel; Spray visualization; Diesel engine performance; Emissions

1. Introduction

Increasing energy demands and more stringent legislation relating to pollutants such as NO_x and CO emissions from fossil fuels have accelerated the use of biodiesel as a fuel. Biodiesel is methyl ester, ethyl ester or fatty acid made from *s* (non-edible and edible oils) such as agricultural waste and animal fat. While particulate matter (PM), unburnt hydrocarbons (UHC) and carbon monoxide (CO) emissions are typically decreased when using biodiesel [1], there are a number of current limitations to using biodiesel as an alternative fuel for compression ignition (CI) engines. Its high viscosity due to its large molecular weight and complex chemical structure [2]; impede complete fuel atomization and combustion; it increases NO_x emissions due to a higher combustion temperatures [1]; and reduces engine performance (lower brake power) [3]. There are a number of different ways that biodiesel performance in CI engines can be improved [4]. Firstly, implementing micro-emulsion technology (where the biodiesel is washed with water and blended with surfactants), although some experimental studies have found that micro-emulsions can cause negative effects on injection systems due to low lubricity and wear corrosion [5]. Another option is exhaust gas recirculation (EGR) or heated of biodiesel, though some experiments have demonstrated that there are some disadvantages such as a significant increase in smoke, PM, UHC, CO emissions, SFC and a reduction in thermal efficiency [6]. These techniques require engine modifications at extra cost. Finally, water can be injected directly into the engine, but there are some drawbacks such as a significant increase in the CO and UHC emissions as well as SFC [3].

Using alcohols as an additive to improve biodiesel properties and combustion efficiency is a promising option [7]. Alcohols such as methanol, ethanol and butanol—derived through biochemical processes from different biomass resources—have a high oxygen content, which helps to promote complete combustion. Particularly, methanol and ethanol with biodiesel have been extensively investigated [8–13]. There are some drawbacks of using these two additives due to unsuitable fuel properties for CI engine design, such as lower values of cetane number (CN), heating value and lubricity. Therefore, researchers have focused on the use of butanol as a suitable blend for CI engines [14]. Butanol presents a number of advantages compared with ethanol, which can improve blends of biodiesel [15,16]: it has higher values of cetane number (25 vs 8), kinematic viscosity (2.63 mm^2/s vs 1.08 mm^2/s) and heating value (33.1 MJ/kg vs 26.8 MJ/kg).

Zaharin et al. [17] reviewed the impact of alcohol-biodiesel blends on CI engine performance and exhaust gas emissions. Firstly, the lower cetane number and higher latent heat of vaporization of alcohols cause a longer ignition delay, produce a higher rate of heat release and lower the in-cylinder pressure. The lower density and viscosity of alcohol improve the spray characteristics and enhance the air–fuel mixing process. The presence of oxygen in alcohols promotes more complete combustion, thereby resulting in an increase of thermal efficiency. Finally, CO, NO_x and PM emissions are decreased. Rakopoulos [18] experimentally studied the combustion and exhaust gas emissions of 20% butanol-80% cottonseed oil and 20% butanol-80% cottonseed biodiesel fuel and compared them to neat cottonseed oil and its neat biodiesel. They found that the presence of butanol reduced the maximum peak in-cylinder pressure, smoke, NO_x and CO emissions, while UHC emissions were increased.

Butanol cannot be produced directly from biological sources. One fermentation pathway produces an acetone–butanol–ethanol (ABE) mixture, typically in the ratio 3:6:1. However, the costs to separate butanol from the ABE mixture are prohibitively expensive, restricting the bio-butanol industry.

Compared to butanol, if an ABE mixture is directly used as an alternative fuel for compression ignition (CI) and spark-ignition (SI) engines, cost of production would be reduced by 40–50% [19–21]. Acetone also has lower boiling point than those of ethanol and butanol (Table 1). Therefore, the acetone vapor is possibly ignited before other species in the blend, which can enhance the conventional fuel's efficiency. Experimental studies have found that adding ABE to conventional diesel enhances the evaporation speed of fuel droplets, reducing droplet lifetime [21]. This has the consequence of increasing thermal efficiency and decreasing combustion temperature, with substantial reduction of soot and NO_x emissions. Another study [22] compared the puffing and micro-exploding behavior of ABE and butanol, concluding that ABE blends enhanced atomization and combustion efficiency.

Table 1
Fuel properties of acetone (A), butanol (B), cottonseed biodiesel (Bd) and diesel (D) [16,21,25].

Properties	A	B	Bd	D
Density (kg/L)	0.971	0.810	0.864	0.82–0.86
Viscosity (mm^2/s) at 40 °C	0.35	2.22	3.7- 4.14	1.9–4.1
Calorific value (MJ/kg)	29.6	33.1	36.8	42.8
Cetane number	–	17-25	52	48
Flash point (°C)	17.8	35	128	74
Boiling point (°C)	56.1	118	280–410	180–400
Latent heat of vaporization (kJ/kg)	501.1	582	230	270
Surface tension (mN/m)	22.6	24.2	32.4	23.8
Flammability limits (vol%)	2.6-12.8	1.4-11.2	–	0.6–5.6

Table 2
Properties of test fules.

Test blends	Density(kg/L)	Viscosity(mm^2/s)	Calorific value(MJ/kg)	Cetane number[a]
D	0.82	2.46	42.6	48
Bd	0.864	4.14	36.8	52
BA	0.795	1.03	31.43	14
BA10Bd90	0.857	3.61	36.26	48
BA20Bd80	0.85	3.246	35.72	44
BA30Bd70	0.843	2.969	35.19	40

[a] CN of tested blends based on estimate for acetone.

Li et al. [23] found that a mixture of butanol and acetone (BA) with ratio 2.9:1 (with no ethanol) can be produced from the fermentation process. This is valuable, due to the drawbacks of using ethanol as an additive fuel for CI engines [8–11]. The impacts of a BA mixture as an additive for diesel fuel have been found to be enhanced spray penetration, reduced exhaust gas emissions (UHC, CO and NO$_x$), and some improvement in brake power (BP) [24,25].

To the authors' knowledge, a BA blend as an additive to biodiesel fuel has not been investigated. The goal of the present study is to investigate the effect of a BA mixture as an additive to cottonseed biodiesel fuel on macroscopic spray characteristics, engine performance and emissions.

2. Fuel preparation and properties

2.1. Gas chromatography analysis of the cottonseed biodiesel (Bd)

A GC–MS analysis of the cottonseed biodiesel (Bd) fuel blend was carried out to determine the chemical profile for the cottonseed biodiesel. The investigation was done using a GC–MS QP 2010 Shimadzu system and a gas chromatograph–mass spectrometer (Fig. S1). The oven temperature of GC was initially set to 30 ºC for 1 min, then increasing at 10 ºC/min to 220 ºC as per the program. The GC–MS results for Bd showed each component with separate peaks (Fig. S2, Table S1).

2.1.1. Blend properties

Normal-butanol (B) and acetone (A) (both at 99.8% analytical grade) were used to produce the BA mixture. Cottonseed biodiesel was prepared from cottonseed oil via transesterification and specification of biodiesel is displayed in section above. A standard test procedure was followed to determine the fatty acid compositions of cottonseed biodiesel, using a GCMS QP2010 Shimadzu system. Diesel was obtained from a local Toowoomba (Australia) petrol station as a baseline. Table 1 shows the properties of the fuel components. The butanol–acetone mixture (BA) was prepared with a ratio of 2.9:1 by volume, which was used to simulate the industrial BA fermentation production. Then BA was blended in three ratios; Table 2 shows the mixtures and the properties of the test blends, measured using ASTM standard procedures. ASTM 1298 was followed to measure the blends' densities, ASTM 445-01 was followed to measure the blends' dynamic viscosities and ASTM D240 was used to measure the blends' heating values.

3. Experimental setup and procedure

3.1. Spray test setup

Figure 1 shows a schematic of the spray characteristics test. Fuel was injected into a constant-volume vessel (CVV) at atmospheric pressure using common-rail injection system with Bosch solenoid 6-hole injector. A Photron SA3 camera with CMOS sensor and exposure time 200 µs was used to

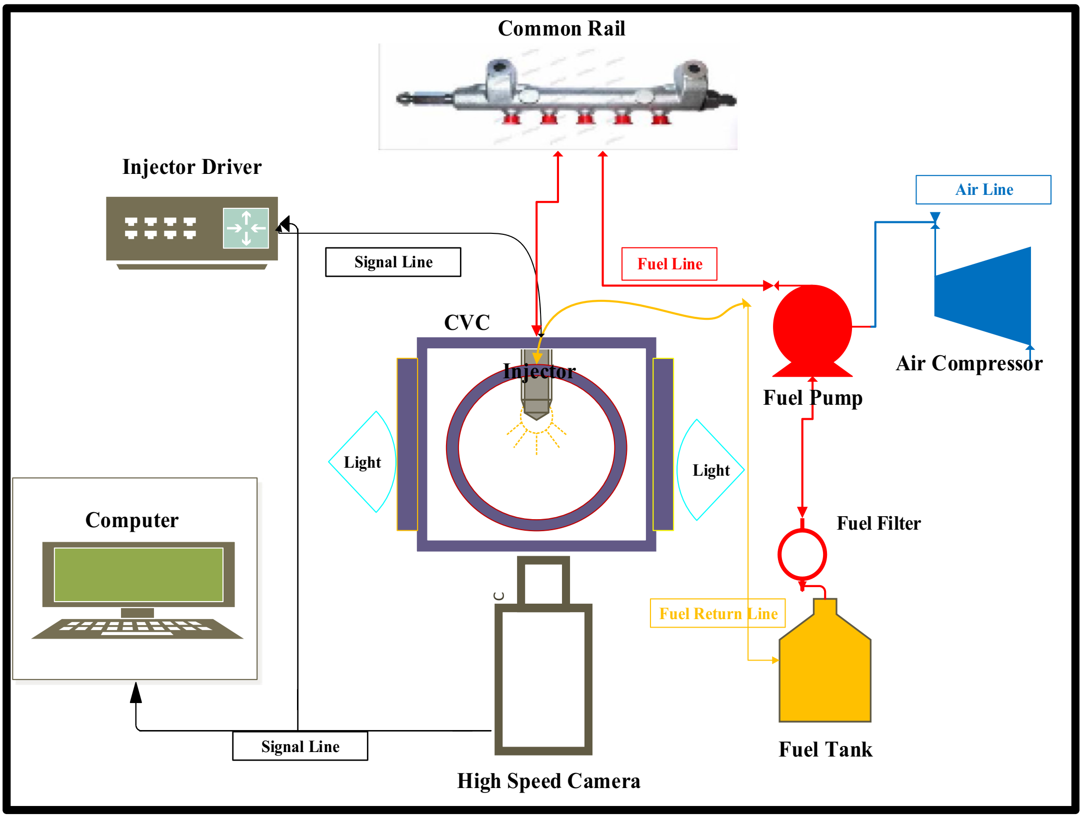


Fig. 1. Schematic of the CVV with common rail fuel injection system setup and camera specification.

Table 3
Specification of injector and injection setup.

Injector type and make	Solenoid, Bosch
Number of nozzles	6 holes
Nozzle diameter (mm)	0.18
Injection pressure (bar)	300–500
Duration of injection (ASOI) (ms)	0.5–1.5
Injection quantity (mg)	12
Enclosed angle (degree)	156
Camera specification	
Camera resolution @ frame rate	1024 × 1024 pixels @ 2000 fps
Lens was connected to the camera	A Nikon AF Micro-Nikkor lens with a focal length of 60 mm
Filter size	62 mm

capture the spray fuel images. LED lights were used for illuminating the CVV. Table 3 contains the injector specifications, camera specification and all spray test conditions. Three tests were performed for each set of parameters.

The spray characteristics (spray penetration and spray cone angle, Fig. 2) were averaged at the same elapsed time and injection conditions. The results of the spray characteristics presented are the average of 6 plumes from each test, further averaged from 3 tests. Complete details regarding the definitions of spray tip penetration and spray cone angle have been reported in previous publications [13,24]. The fuel spray shape is assumed to be a cone with a hemisphere on the end, so the spray volume can be calculated to be [13,24]:

$$V = \left(\frac{\pi}{3}\right)S^3\left[\tan^2(\theta)\right]\frac{1+2\tan\left(\frac{\theta}{2}\right)}{\left[1+\tan\left(\frac{\theta}{2}\right)\right]^3} \quad (1)$$

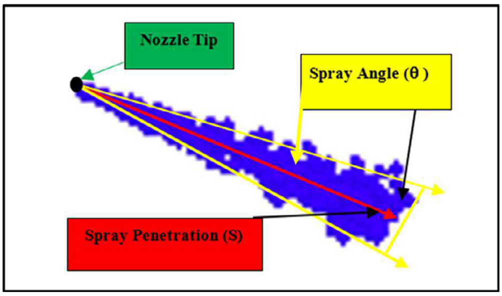


Fig. 2. Spray penetration (S) and spray cone angle (θ) definitions.

Table 4
Engine specifications and test conditions.

Engine specifications	
Compression ratio	5:1-19:1
Number of cylinders	1
Bore (mm)	90
Stroke (mm)	74
Test conditions	
Engine speeds (rpm) at full load	1400, 2000 and 2600
Compression ratio	18:1

ASOI refers to the interval between the signal for injection to commence and when these images were captured. The spray images were processed in three steps using a similar method reported in previous publications [13,24]. Figures S3 and S4 show the spray image processing methodology.

3.2. *Engine test setup*

A G.U.N.T. variable compression, single-cylinder, four-stroke, water-cooled diesel engine was used (Fig. 3). Direct injection (DI) was used using a mechanical injector with three holes and an injection pressure of 300 bar. The Engine specification and test setup are listed in Table 4. The engine load was controlled using an electrical dynamometer connected to the engine. A crank angle encoder was used to measure crank angles connected on the engine shaft. A pressure transducer (Kistler 6052C) was inserted in the cylinder head to record the in-cylinder pressure values for fifty cycles each test. The Exhaust gas temperature (EGT) was measured using a thermocouple transducer inserted in the exhaust system. NO_x, CO and UHC emissions were measured using a Coda gas analyzer. More details in relation to the accuracy ranges of engine equipment and the Coda gas analyzers have been reported in previous publications [24,25]. Because of the experiments run in the same ambient conditions, the influence of environment on the diesel engine test was ignored. The engine was heated up until stable conditions were reached, with error bars showing the range of measurements.

3.3. *Statistical analysis*

The experimental data of the spray characteristics, engine performance and exhaust gas emissions were analyzed using SPSS. One-way ANOVA and Bonferroni post-hoc tests were performed to study the differences between the fuel types for S, θ, BP, SFC, NO_x, CO and UHC at a significance level of $p < 0.05$ [26]. The results of these tests are included in Tables S2–S5 and Fig. S6 in the Supplemental material.

4. Results of spray characteristics and discussion

The main drawback of biodiesel is its higher viscosity and higher surface tension (Table 1), which results in a reduction of injection velocity. Another drawback of the high viscosity of biodiesel is the higher injection pressure required to overcome the friction force from contact between the nozzle wall and fuels in order to avoid a lower injection rate [17]. Therefore, there is an insufficient reaction rate leading to reduced engine power and increased fuel consumption as a consequence of using biodiesel. The spray evolution and development of all test fuels are qualitatively the same for each after start of injection (ASOI) moment and both injection pressures (Fig. 4). There is a moderate influence of injection pressure on spray penetration and a much larger influence of duration (ASOI). A higher injection pressure forces the liquid fuel to leave the nozzle within turbulent flow, assisting the outer boundaries of the sprayed fuel to break up into droplets [27].

Including BA in the mixture improves the spray penetration of biodiesel cottonseed fuel (Fig. 5) due to the decreased viscosity. In addition, the improvement in spray penetration, which results in an increased air–fuel mixing rate [24]. Moreover, Kim et al. [28] found that cottonseed biodiesel can only be vaporized completely when the temperature exceeded 500 °C due to its higher boiling point. Adding BA, with its lower boiling point temperature, could reduce droplet lifetime, thereby enhancing spray vaporization. The increased spray penetration of the BA-biodiesel blends was statistically significant (refer to Table S3).

These findings are consistent with Zaharin et al. [17] who stated that the low density and viscosity of alcohol improve spray characteristics and enhance the air–fuel mixing process of biodiesel [24].

The spray cone angle was slightly reduced as a result of adding BA to neat biodiesel (Fig. 4). Biodiesel generally has the highest spray cone angle due to its high viscosity [17]. The spray volume of the BABd blends was generally highest (Fig. 6).

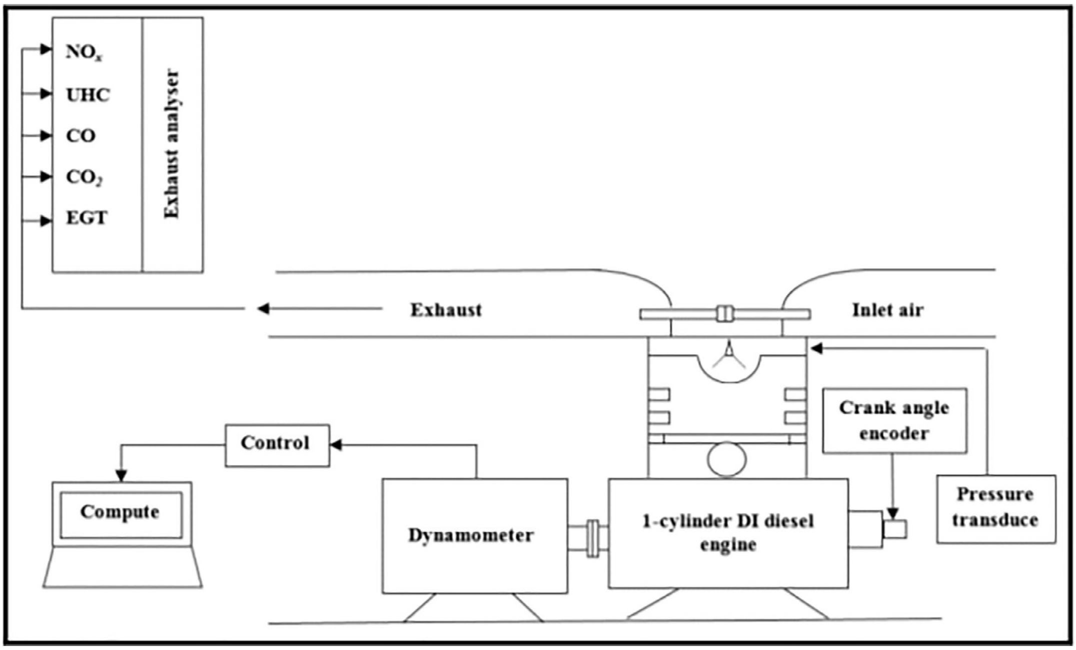


Fig. 3. Schematic diagram of test set-up.

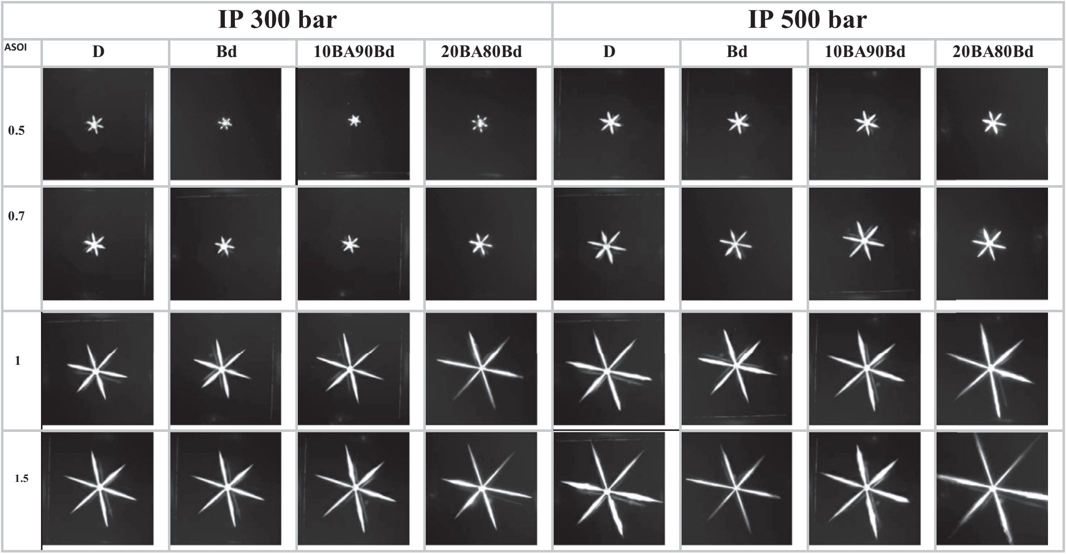


Fig. 4. Spray comparison images of test fuel blends.

5. Results of engine performance and discussion

5.1. Combustion characteristics

Figure 7 presents the behavior of the in-cylinder pressure trace and heat release rate (HRR) of the test fuels at 2000 rpm engine speed. Diesel had the highest peak in-cylinder pressure, in agreement with Nabi et al. [5] where the peak in-cylinder pressure of biodiesel was 12% less than that of neat diesel. The peak in-cylinder pressure of biodiesel and its blends tends to be lower due to the higher fuel viscosity slowing the mixing rate of air and fuel [10], as well as its heating value being lower than diesel (36.8 vs 42.8 (MJ/kg)). Although alcohols have a low heating value, HRR$_{max}$ of the

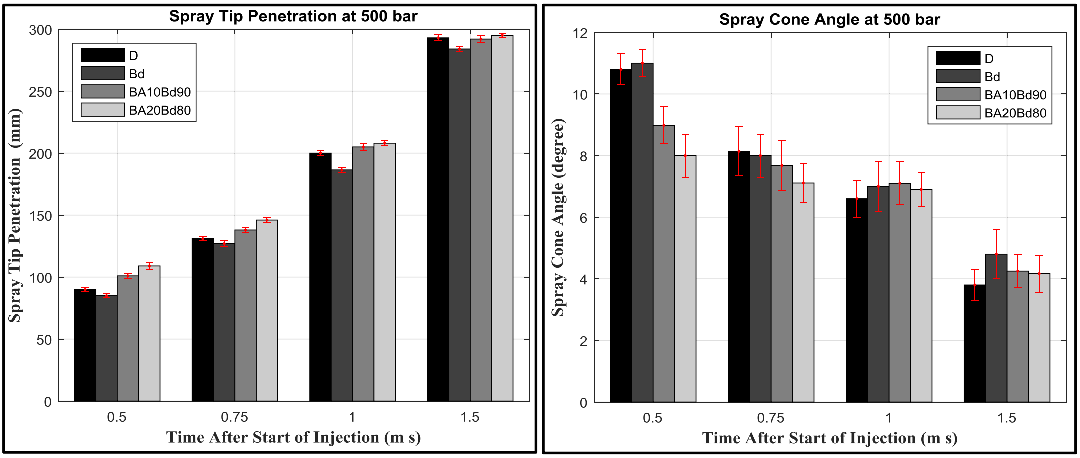


Fig. 5. Spray penetration (left) and spray cone angle (right) for test fuel blends.

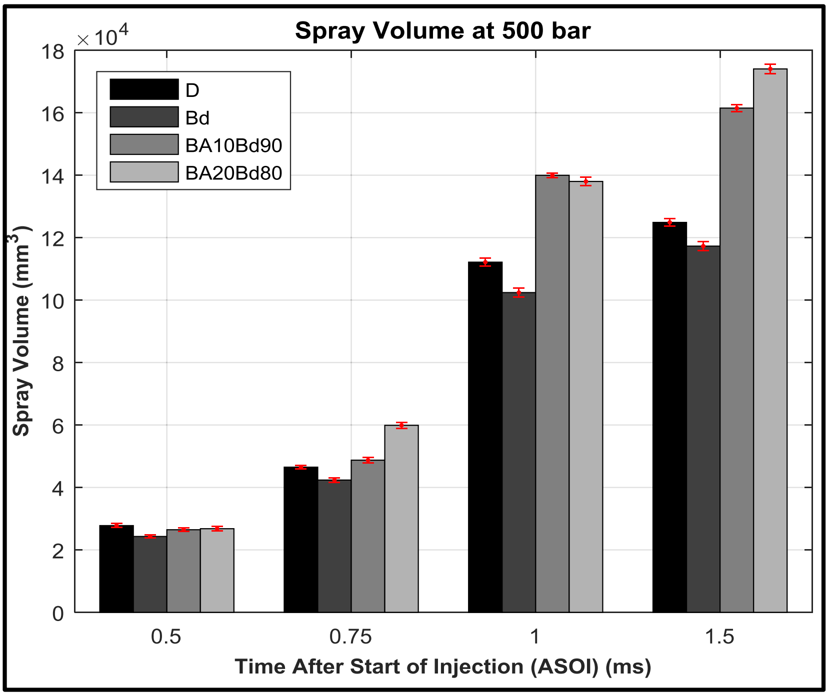


Fig. 6. Spray volume for test fuel blends.

alcohol blends are higher than D100. The reason is that the oxygen content of the alcohols is higher. The lower LHV of alcohols may become an obstacle to achieving maximum in-cylinder pressure and torque under full load condition, thereby resulting in reduced engine power.

Adding small amounts of BA to the mixture increased the ignition time due to its lower CN and the higher latent heat value and boiling point, which consequently improved the fuel–air mixing and evaporation rate (Figs. 3–5) and lead to rapid combustion.

The reduced energy in the biofuel blends lowered the peak in-cylinder pressure compared to diesel; however, BA30Bd70 produced a higher peak in-cylinder pressure than neat biodiesel. The HRR trace is consistent with Ref. [28]. Corresponding to its high peak cylinder pressure, the BA30Bd70 blend showed the highest peak HRR of all the test fuels.

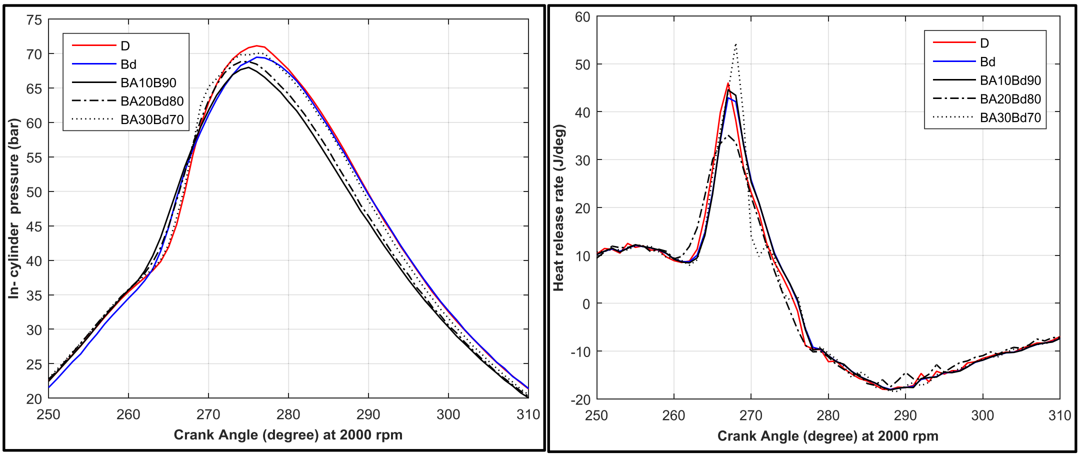


Fig. 7. In-cylinder pressure (left) and HRR (right) for all blends of fuel at engine speed 2000 rpm.

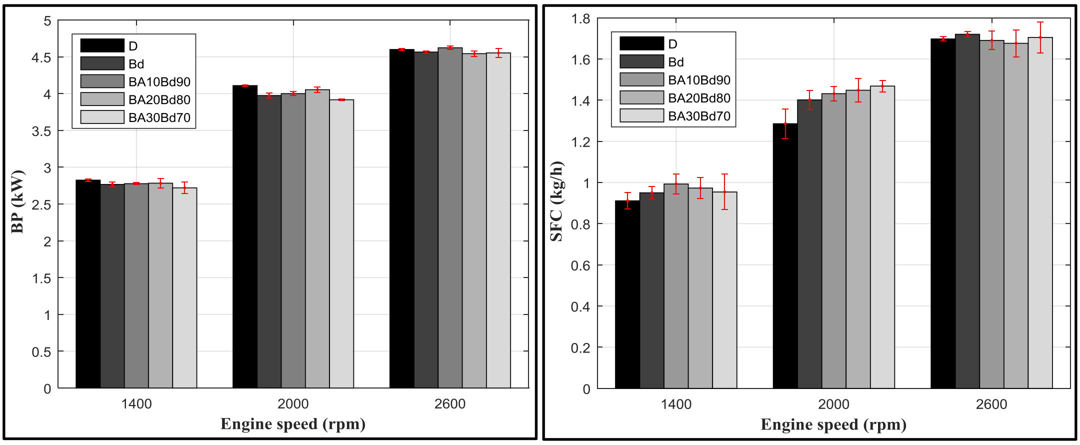


Fig. 8. BP (left) and SFC (right) of test fuels at three engine speeds.

5.2. Engine performance characteristics

The summary of the descriptive statistics tests is presented in the Supplemental material. The behavior of each studied parameter for the different studied fuels at different engine speeds is presented and discussed separately in detail in the following subsections.

Figure 8 shows the variation of BP and SFC with the engine speeds of the test fuels. It is observed that the BP of all the biofuels were generally slightly lower than neat diesel. The SFC of the BA-biodiesel blends were slightly higher than that of neat biodiesel due to the lower heating value of the BA blend fuel (Table 2); thus, it requires a higher volume of fuel to produce the same engine power [29]. Table S3 shows no significant difference between the fuels in regard to BP and SFC.

5.3. Emissions characteristics

Neat biodiesel produced higher amounts of NO_x than neat diesel (Fig. 9), in agreement with the vast majority of previous studies [2,29–31]. This increase is mainly due to the higher combustion temperature and different injection characteristics [10]. The addition of BA slightly reduced NO_x due to the low boiling point of BA and consequent combustion temperature reduction. Acetone and butanol have much lower boiling points compared to biodiesel, therefore it is quite possible that bubbles formed in the fuel droplet because of this drastic fuel property difference and finally induced a micro explosion. This reduction in NO_x is not significant as reported in Table S5, although the NO_x levels were still somewhat higher than those of neat diesel.

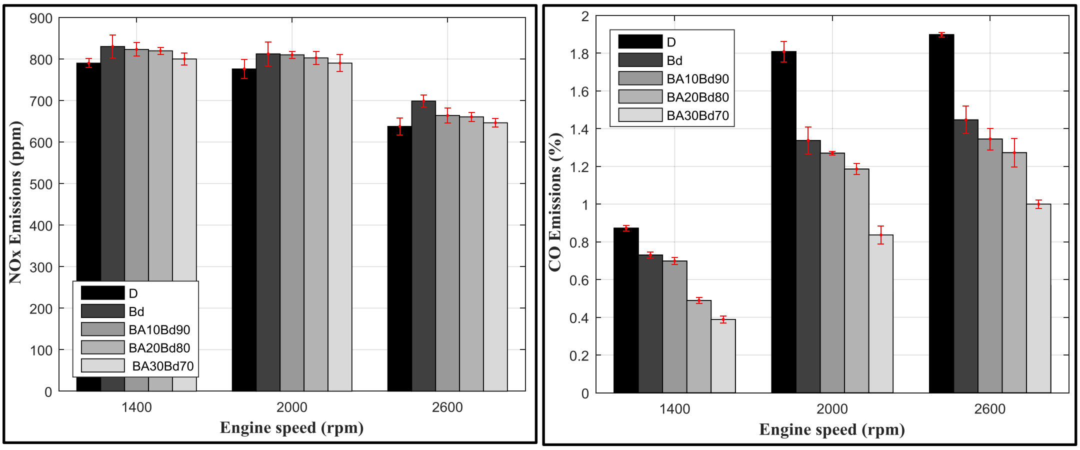


Fig. 9. NO_x (left) and CO emissions (right) of test fuels at three engine speeds.

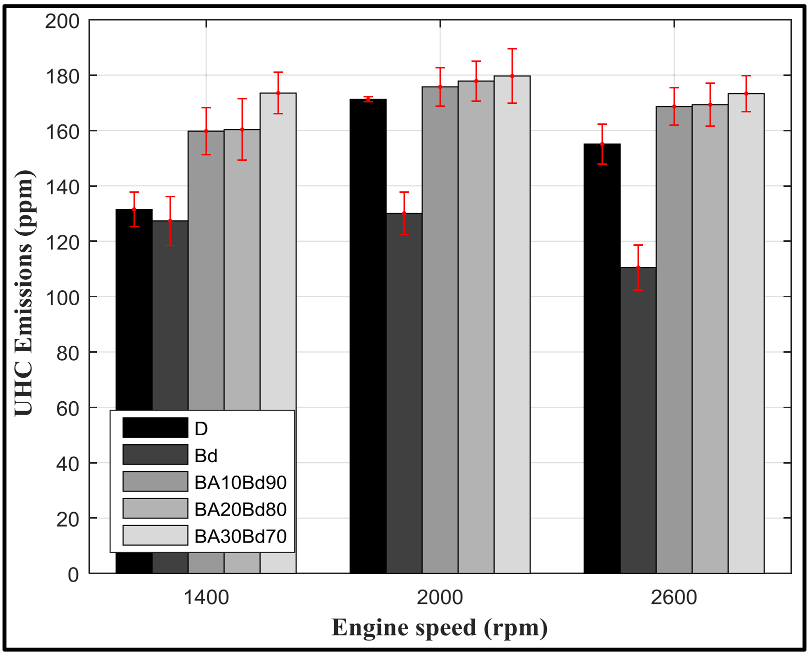


Fig. 10. UHC emissions of test fuels at three engine speeds.

Figure 9 shows that neat biodiesel produces lower CO emissions than neat diesel (consistent with Refs. [5,10]) and increasing the amount of BA further reduced the CO emissions by a significant margin (Table S5). This is principally due to the higher oxygen content and the lower carbon to hydrogen ratio in the BA mixture and biodiesel blends (Table 1) compared to neat diesel.

The use of BA-biodiesel blends increased the UHC emissions compared to neat diesel at all engine speeds (Fig. 10). This increment occurred because n-butanol and acetone have high heats of vaporization (Table 1), which results in insufficient time for completing the reaction. Although the usage of neat biodiesel significantly reduced UHC emissions compared to neat diesel, the addition of BA significantly increased the UHC emissions (Table S5). These results are in agreement with Ref. [17]. Xue et al. [2] reported that 89.5% of research found that neat biodiesel produced lower UHC emissions than neat diesel.

6. Conclusions

This experimental study investigated the impact of using a butanol–acetone (BA) mixture as an additive to biodiesel. The spray experiments were conducted in a CVV at atmospheric conditions. The macroscopic spray characteristics (spray penetration, spray cone angle and spray volume) of the test fuels were measured. The engine test experiments were also carried out in a single-cylinder DI diesel engine. The engine performance and exhaust gas emissions of the test fuel blends were assessed and compared. The experimental data of the spray characteristics, engine performance and exhaust gas emissions were analyzed using SPSS.

The peak in-cylinder pressure of all the biofuels was lower than neat diesel, but BA30Bd70 contained sufficient BA to have a higher peak in-cylinder pressure than neat biodiesel. However, the BP was slightly lower and the SFC was higher for all biofuels compared to conventional diesel because the heating values of BA-biodiesel blends are lower. NO_x emissions were decreased by 7% for all BA-biodiesel blends compared to neat biodiesel at all engine speeds, accounting for some of the increase caused by neat biodiesel. CO emissions for neat biodiesel were significantly reduced by 40% compared to neat diesel and increasing levels of BA significantly reduced the CO emissions further. However, UHC emissions were slightly increased as a result of adding the BA mixture compared to neat biodiesel and diesel.

The BA mixtures are an eco-friendly alternative fuel blend produced from biomass. The intermediate fermentation product of butanol should soon be given more attention as an alternative fuel blend. These alcohols can easily be blended with biodiesel in any percentage with no phase separation. Using a BA mixture as an additive to biodiesel results in a blend with generally improved properties. However, acetone has a much higher volatility than diesel, so that 30% BA is not safe in long-term storage in a diesel fuel tank at room temperature, while 20% BA is safe up to 40 °C, which is not generally acceptable. The 10% BA blend is safe up to 56 °C. Using BA with low purity as an additive to diesel or biodiesel could additionally reduce the BA production cost.

Acknowledgments

The first author thanks the Iraqi Government Ministry of Higher Education and Scientific Research for supporting the research. The authors are also grateful to Rachel King for her assistance with the statistical analysis, Rishabh Choudhury for his assistance with the spray experiments, Friederike Susette Eberhard for her assistance with the GC–MS analysis, Brian Lenske for his assistance with the engine experiments, Daniel McIntyre from Diesel Care Australia Pty Ltd, Toowoomba branch for his discussion and advice related to the common rail injection system.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi: 10.1016/j.proci.2018.08.035.

References

[1] M.S. Koçak, E. Ileri, Z. Utlu, *Energ Fuels* 21 (6) (2007) 3622–3626.

[2] J. Xue, T.E. Grift, A.C. Hansen, *Renew. Sustain. Energy Rev.* 15 (2) (2011) 1098–1116.

[3] S. Ramalingam, S. Rajendran, P. Ganesan, *Renew. Sustain. Energy Rev.*, 81(2018) 3215–3222.

[4] E. Jiaqiang, M. Pham, D. Zhao, et al., *Renew. Sustain. Energy Rev.* 80 (2017) 620–647.

[5] M.N. Nabi, M.M. Rahman, M.S. Akhter, *Appl. Therm. Eng.* 29 (11) (2009) 2265–2270.

[6] V. Pradeep, R. Sharma, *Renew. Energy* 32 (7) (2007) 1136–1154.

[7] Y.-C. Chang, W.-J. Lee, T.S. Wu, C.-Y. Wu, S.-J. Chen, *Energy*, 64(2014) 678–687.

[8] S. Kumar, J.H Cho, J. Park, I. Moon, *Renew. Sustain. Energy Rev.* 22 (2013) 46–72.

[9] S.A. Shahir, H.H. Masjuki, M.A. Kalam, A. Imran, A.M. Ashraful, *Renew. Sustain. Energy Rev.* 48 (2015) 62–78.

[10] K.N. Gopal, B. Ashok, K.S. Kumar, et al., *Biofuels* 9 (2017) 1–8.

[11] H. Tse, C.W. Leung, C.S. Cheung, *Energy* 83 (2015) 343–350.

[12] C. Jin, M. Yao, H. Liu, C.-F.F. Lee, J. Ji, *Renew. Sustain. Energy Rev.* 15 (8) (2011) 4080–4106.

[13] S.J.M. Algayyim, A.P. Wandel, T. Yusaf, *Energies*,11(5) 1298–1310.

[14] T. Laza, Á. Bereczky, *Fuel* 90 (2) (2011) 803–810.

[15] N. Yilmaz, F.M. Vigil, K. Benalil, S.M. Davis, A. Calva, *Fuel* 135 (2014) 46–50.

[16] P. Weerachanchai, C. Tangsathitkulchai, M. Tangsathitkulchai, *World Acad. Sci. Eng. Technol.* 56 (2009) 387–393.

[17] M.S.M. Zaharin, N.R. Abdullah, G. Najafi, H. Sharudin, T. Yusaf, *Renew. Sustain. Energy Rev.* 79 (2017) 475–493.

[18] D.C. Rakopoulos, *Fuel* 105 (2013) 603–613.

[19] Y. Ni, Z. Sun, *Appl. Microbiol. Technol.* 83 (3) (2009) 415.

[20] M.H. Abd-Alla, A.N Zohri, A. W.El-Enany, S.M. Ali, *Anaerobe* 32 (2015) 77–86.

[21] S.J.M Algayyim, A.P. Wandel, T. Yusaf, I. Hamawand, *Renew. Sustain. Energy Rev.* 82 (2018) 1195–1214.

[22] D.C.K. Rao, S. Karmakar, S.K. Som, *Combust. Sci. Technol.* 189 (2017) 1–17.

[23] X. Li, Z.-G. Li, Z.-P. Shi, *Bioresour. Bioprocess.* 1 (1) (2014) 1–13.

[24] S.J. M.Algayyim, A.P. Wandel, T. Yusaf, I. Hamawand, *Energy* 140 (2017) 1074–1086.

[25] S.J. M.Algayyim, A.P. Wandel, T. Yusaf, S.H. Al-lwayzy, I. Hamawand, *Fuel* 227 (2018) 118–126.

[26] S.H. Al-lwayzy, T. Yusaf, *Renew. Energy* 101 (2017) 690–701.

[27] H.K. Suh, C.S Lee, *Renew. Sustain. Energy Rev.* 58 (2016) 1601–1620.

[28] H.J. Kim, H.K. Suh, S.H. Park, C.S. Lee, *Energy Fuels* 22 (3) (2008) 2091–2098.

[29] B.S. Chauhan, N. Kumar, H.M Cho, H.C. Lim, *Energy* 56 (2013) 1–7.

[30] Z.-H. Zhang, R. Balasubramanian, *Appl. Energy* 163 (2016) 71–80.

[31] G. Dhamodaran, R. Krishnan, Y.K. Pochareddy, H.M. Pyarelal, H. Sivasubramanian, A.K. Ganeshram, *Fuel* 187 (2017) 296–305.

7.2 Summary of Article VI

Chapter 7 investigated the impact of a BA-cottonseed biodiesel blend on spray behaviour and engine performance under various blend ratios and different operating conditions. All experimental results were compared to conventional diesel at similar environmental and operating conditions. The experimental data were statistically analysed using SPSS software. The result showed that all biofuel (BA-biodiesel) blends had lower in-cylinder pressure compared to that of neat diesel, while high ratios of BA in test blends produced higher in-cylinder pressure than neat biodiesel. Specific fuel consumption was increased for all biofuel blends due to their lower calorific value. Some reduction was found in NO_x emissions as a result of adding BA to neat biodiesel due to BA's low combustion temperature. There was a significant reduction in CO emissions of all BA-biodiesel blends, while UHC emissions were increased. Using a BA mixture as an additive to biodiesel results in a blend with generally improved properties.

Conclusions

This study evaluated and compared the effect of using butanol-acetone (BA) additives with D and Bd on macroscopic spray characteristics, engine performance and emission concentration. Spray tests were carried out in a CVV under different injection conditions (injector hole diameter, injection duration, injection pressure and ambient conditions). A high-speed camera was used to record spray images. The spray's edge was determined using an automatic threshold calculation algorithm to locate the spray outline (edge) from the binary images. Macroscopic spray characteristics (spray penetration, spray cone angle and spray volume) were measured.

In addition, engine tests were conducted using a single-cylinder DI diesel engine at three engine speeds and two compression ratios (18:1 and 19:1) at full load. The engine's performance was evaluated using in-cylinder pressure, BP, BSFC, BTE, EGT and HRR. Emission characteristics (NO_x, UHC, CO and CO_2) were also measured and analysed. The experimental data were statistically assessed using ANOVA to evaluate whether variations in parameters due to the different fuels were significant.

Chapter 2 summarised and revised the production and application of ABE blend: A decade ago, the commercial production of ABE via the fermentation of biomass was not feasible due to the low ABE yield. Nowadays, some improvements are occurring as a result of developments in genetic engineering and pre-treatment processes. These improvements have led to an increase in ABE yield, making ABE a potential blend for both diesel and gasoline fuels. A butanol blend is more beneficial in diesel engines compared to ethanol. The ABE blend potentially has the same benefits as neat butanol, while being less expensive to produce. Another intermediate of butanol that can be produced without ethanol (which is detrimental to CI engine performance) is BA in a ratio of 2.9:1. There are limited studies related to BA blended in neat D and Bd including spray characteristics, engine performance and emissions. Furthermore, there is a lack of studies regarding iso-BA or n-BA with neat diesel. There is a lack of studies regarding the dual blend of iso-BA and n-BA with neat D. Finally, there is a lack of studies related to low purity ABE and BA blends tested in CI or SI engines.

Spray behaviour is among the most important factors that affects CI engines' performance and emission levels. Fuel flow visualisation and optical diagnostics have been widely employed as methods for investigating combustion processes in CI engines. Due to the increase in the number of renewable alternative fuels and more stringent legislation governing engine pollutant emissions, it is important to characterise the spray behaviour of these alternative fuels in CI engines under different operating conditions. Therefore, **Article II (Chapter 3)** studied the impact of different operating conditions such as injector hole diameter, injection pressure and injection duration in addition to various blend ratios on spray characteristics. The spray image analysis showed that the spray penetration length was increased with larger injector hole diameter and higher injection pressure. The spray penetration of the 20% butanol-80% diesel (B20D80) blend was slightly further than that of neat D because the butanol reduces the viscosity. The spray penetration of the test fuel blends becomes longer while the spray cone angle was slightly widened via the increase in either injection pressure or hole diameter. The spray volume of all the test fuels was increased as a result of increased hole diameter or injection pressures, which results in increased contact surface area between air and fuel, thereby resulting in increased mixing rate, atomisation and vaporisation rate and combustion efficiency. In conclusion, controlling injection characteristics of the injector in CI engines could lead to more efficient mixing between the injected fuel and spray propagation. Thus, additional advantages can be gained to achieve an efficient diesel engine performance, especially when using promising alternative fuels like bio-alcohol blended with diesel.

Many researchers have investigated the fermentation process to produce a fuel mixture of ABE with a 3:6:1 ratio. In a study by Li et al. (2014), BA was produced via fermentation of cassava substrate with a ratio of 2.9:1. BA with no ethanol is a better additive for diesel than ABE, because ethanol has corrosion behaviour in fuel injection system. Therefore, a BA blend could be a good additive blend to diesel compared to ABE. In **Chapter 4**, it was found that there was no visual separation of components in BA-D blends: they are inherently stable over a four-month period. The peak in-cylinder pressure was higher using 20% BA in diesel. The combustion phasing advanced with increasing BA content. This can improve the combustion quality because of reduced combustion duration as a result of the low CN. This further resulted in maximum HRR when testing the oxygenated additive fuel blends in CI engines. BP was maximum at 10% BA at all engine speeds, approximately 4-5% higher than D100. The BTE of 10BA90D was comparable with D100 at all engine speeds, but was slightly increased by 6% and 8% at all engine speeds when the BA ratio was 20% and 30% respectively. EGT, NO_x and CO emissions of all BA-D blends were reduced as a result of blended BA with neat diesel. BA is a good renewable fuel additive to diesel because it can be fermented from non-edible biomass feedstock and without requiring a recovery process to obtain a neat chemical. It can improve energy efficiency and reduce pollutant emissions.

There are four different isomers of butanol: normal (n-B), iso-butanol (iso-B), sec-butanol (sec-B) and tert-butanol (tert-B). Sec-B and tert-B are not established in the butanol fermentation industry. N-butanol and iso-butanol have been widely investigated in diesel engines. Therefore, iso-BA or n-BA in diesel blends could be beneficial in informing the BA industry which butanol isomer should be produced. **Article IV** (**Chapter 5**) found that the spray penetration of iso-BA was slightly shorter than that of n-BA, while the spray cone angle of both butanol isomers was not changed significantly. Iso-BA-D blends showed higher in-cylinder pressure and BP, while n-BA-D blends produced lower emission levels of NO_x and UHC.

Therefore, using n-B and iso-B blended together as an additive for diesel fuel could be a suitable blend to obtain optimum results in regard to engine performance and could be a good alternative as an additive fuel that could soon be utilised. In **Article V (Chapter 6),** it was found that the 10% dual blend (compared to neat diesel) produced some improvement in BP and comparable values of in-cylinder pressure. The higher ratio of iso-B possibly produced the best CO reduction while the high ratio of the n-B blend produced the best overall reduction in UHC and NO_x emissions.

The high viscosity of biodiesel resulted in obstacles to atomisation and complete combustion, while biodiesel combustion produces high combustion temperature which releases high NO_x emissions. Therefore, blending BA with biodiesel could result in improved properties of biodiesel. The engine tests of **Article VI (Chapter 7)** revealed that high BA-biodiesel blend ratios have a higher peak in-cylinder pressure than neat biodiesel. However, the BP was slightly lower and the SFC was higher for all biofuels compared to conventional diesel because the heating values of BA-biodiesel blends are lower. NO_x emissions were decreased by 7% for all BA-biodiesel blends compared to neat biodiesel at all engine speeds, accounting for some of the increase caused by neat biodiesel. CO emissions for neat biodiesel were significantly reduced by 40% compared to neat diesel and increasing levels of BA significantly reduced the CO emissions further. However, UHC emissions were slightly increased as a result of adding the BA mixture compared to neat biodiesel and diesel. These alcohols can easily be blended with biodiesel in any percentage with no phase separation. Using a BA mixture as an additive to biodiesel results in a blend with generally improved properties.

The results in this thesis support the notion that a BA blend is promising as an alternative, renewable, environmentally-friendly additive to neat diesel and biodiesel without diesel engine modification, that can enhance spray characteristics and engine performance and reduce diesel engine emissions.

The following suggestions are recommended as additional investigations to assist industry in focussing its efforts on producing the variety of ABE or BA which yields the best results.

1. Comparative study of engine performance of ABE, isopropanol-n-butanol-ethanol (IBE) and BA-D blends under various blend ratios and operating conditions.
2. Spray characteristics and engine performance of BA with water as additive to neat diesel.
3. Spray characteristics and engine performance of BA-biodiesel-diesel blend.
4. Engine performance of BA-petrol blend in SI engine under various blend ratios and operating conditions.
5. Engine performance of hydrated BA and petrol blend.
6. Effects of BA additive on the fuel system and long-term durability/reliability of the CI and SI engines.
7. How the bio-alcohol mixture should be blended for CI and SI engines to produce the best engine performance and fewest emissions also needs to be investigated.

References

Algayyim, S, Wandel, AP & Yusaf, T, 2018, 'The Impact of Injector Hole Diameter on Spray Behaviour for Butanol-Diesel Blends', *Energies*, vol. 11, no. 5, p. 1298.

Algayyim, SJM, Wandel, AP, Yusaf, T & Hamawand, I, 2017, 'The impact of n-butanol and iso-butanol as components of butanol-acetone (BA) mixture-diesel blend on spray, combustion characteristics, engine performance and emission in direct injection diesel engine', *Energy*, vol. 140, no. Part 1, pp. 1074-86.

Algayyim, SJM, Wandel, AP, Yusaf, T & Al-Lwayzy, S, 2018, 'Butanol–acetone mixture blended with cottonseed biodiesel: Spray characteristics evolution, combustion characteristics, engine performance and emission', *Proceedings of the Combustion Institute*, vol. 37, pp. 1-11.

Algayyim, SJM, Wandel, AP, Yusaf, T & Hamawand, I, 2018, 'Production and application of ABE as a biofuel', *Renewable and Sustainable Energy Reviews*, vol. 82, Part 1, pp. 1195-214.

Algayyim, SJM, Wandel, AP, Yusaf, T, Al-Lwayzy, S & Hamawand, I, 2018, 'Impact of butanol-acetone mixture as a fuel additive on diesel engine performance and emissions', *Fuel*, vol. 227, pp. 118-26.

Campos-Fernández, J, Arnal, JM, Gómez, J & Dorado, MP, 2012, 'A comparison of performance of higher alcohols/diesel fuel blends in a diesel engine', *Applied Energy*, vol. 95, pp. 267-75.

Doğan, O, 2011, 'The influence of n-butanol/diesel fuel blends utilization on a small diesel engine performance and emissions', *Fuel*, vol. 90, no. 7, pp. 2467-72.

Emiroğlu, AO & Şen, M, 2018, 'Combustion, performance and emission characteristics of various alcohol blends in a single cylinder diesel engine', *Fuel*, vol. 212, pp. 34-40.

Erski, T, 2014, *Compares current and projected energy consumption between OECD and non-OECD member countries,* viewed 19 February 2014, <https://youtu.be/bVVkhvZYM74>.>.

Hansen, A, Gratton, M & Yuan, W, 2006, 'Diesel engine performance and NO_x emissions from oxygenated biofuels and blends with diesel fuel', *Transactions of the ASABE*, vol. 49, no. 3, pp. 589-95.

Hansen, AC, Zhang, Q & Lyne, PWL, 2005, 'Ethanol–diesel fuel blends — a review', *Bioresource Technology*, vol. 96, no. 3, pp. 277-85.

Jin, C, Yao, M, Liu, H, Lee, CF & Ji, J, 2011, 'Progress in the production and application of n-butanol as a biofuel', *Renewable and Sustainable Energy Reviews*, vol. 15, no. 8, pp. 4080-106.

Jin, C, Yao, M, Liu, H, Lee, CF & Ji, J, 2011, 'Progress in the production and application of n-butanol as a biofuel', *Renewable and Sustainable Energy Reviews*, vol. 15, no. 8, pp. 4080-106.

Joy, N, Devarajan, Y, Nagappan, B & Anderson, A, 2018, 'Exhaust emission study on neat biodiesel and alcohol blends fueled diesel engine', *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 40, no. 1, pp. 115-9.

Juan, JC, Kartika, DA, Wu, TY & Hin, TY, 2011, 'Biodiesel production from jatropha oil by catalytic and non-catalytic approaches: an overview', *Bioresource Technology*, vol. 102, no. 2, pp. 452-60.

Koçak, MS, Ileri, E & Utlu, Z, 2007, 'Experimental study of emission parameters of biodiesel fuels obtained from canola, hazelnut, and waste cooking oils', *Energy & Fuels*, vol. 21, no. 6, pp. 3622-6.

Kumar, S, Cho, JH, Park, J & Moon, I, 2013, 'Advances in diesel–alcohol blends and their effects on the performance and emissions of diesel engines', *Renewable and Sustainable Energy Reviews*, vol. 22, pp. 46-72.

Laza, T & Bereczky, Á, 2011, 'Basic fuel properties of rapeseed oil-higher alcohols blends', *Fuel*, vol. 90, no. 2, pp. 803-10.

Li, X, Li, Z-G & Shi, Z-P, 2014, 'Metabolic flux and transcriptional analysis elucidate higher butanol/acetone ratio feature in ABE extractive fermentation by Clostridium acetobutylicum using cassava substrate', *Bioresources and Bioprocessing*, vol. 1, no. 1, pp. 1-13.

Lujaji, F, Bereczky, A, Janosi, L, Novak, C & Mbarawa, M, 2010, 'Cetane number and thermal properties of vegetable oil, biodiesel, 1-butanol and diesel blends', *Journal of Thermal Analysis and Calorimetry*, vol. 102, no. 3, pp. 1175-81.

No, S-Y, 2011, 'Inedible vegetable oils and their derivatives for alternative diesel fuels in CI engines: a review', *Renewable and Sustainable Energy Reviews*, vol. 15, no. 1, pp. 131-49.

Qureshi, N, Saha, BC, Hector, RE, Dien, B, Hughes, S, Liu, S, Iten, L, Bowman, MJ, Sarath, G & Cotta, MA, 2010, 'Production of butanol (a biofuel) from agricultural residues: Part II – Use of corn stover and switchgrass hydrolysates', *Biomass and Bioenergy*, vol. 34, no. 4, pp. 566-71.

Satgé de Caro, P, Mouloungui, Z, Vaitilingom, G & Berge, JC, 2001, 'Interest of combining an additive with diesel–ethanol blends for use in diesel engines', *Fuel*, vol. 80, no. 4, pp. 565-74.

Savaliya, ML, Dhorajiya, BD & Dholakiya, BZ, 2013, 'Recent advancement in production of liquid biofuels from renewable resources: a review', *Research on Chemical Intermediates*, vol. 41, no. 2, pp. 475-509.

Sayin, C, 2010, 'Engine performance and exhaust gas emissions of methanol and ethanol–diesel blends', *Fuel*, vol. 89, no. 11, pp. 3410-5.

Shahir, SA, Masjuki, HH, Kalam, MA, Imran, A & Ashraful, AM, 2015, 'Performance and emission assessment of diesel–biodiesel–ethanol/bioethanol blend as a fuel in diesel engines: A review', *Renewable and Sustainable Energy Reviews*, vol. 48, pp. 62-78.

Tse, H, Leung, CW & Cheung, CS, 2015, 'Investigation on the combustion characteristics and particulate emissions from a diesel engine fueled with diesel-biodiesel-ethanol blends', *Energy*, vol. 83, pp. 343-50.

Weerachanchai, P, Tangsathitkulchai, C & Tangsathitkulchai, M, 2009, 'Phase behaviors and fuel properties of bio-oil–diesel–alcohol blends', *World Academy of Science, Engineering and Technology*, vol. 56, pp. 387-93.

Wu, H-W & Wu, Z-Y, 2013, 'Using Taguchi method on combustion performance of a diesel engine with diesel/biodiesel blend and port-inducting H 2', *Applied Energy*, vol. 104, pp. 362-70.

Xue, J, Grift, TE & Hansen, AC, 2011, 'Effect of biodiesel on engine performances and emissions', *Renewable and Sustainable Energy Reviews*, vol. 15, no. 2, pp. 1098-116.

Yilmaz, N, Vigil, FM, Benalil, K, Davis, SM & Calva, A, 2014, 'Effect of biodiesel–butanol fuel blends on emissions and performance characteristics of a diesel engine', *Fuel*, vol. 135, pp. 46-50.

Zannis, TC, Pariotis, EG, Hountalas, DT, Rakopoulos, DC & Levendis, YA, 2007, 'Theoretical study of DI diesel engine performance and pollutant emissions using comparable air-side and fuel-side oxygen addition', *Energy Conversion and Management*, vol. 48, no. 11, pp. 2962-70.

Appendix A: Poster Abstract and Conference Paper

The major outcomes of this study were also presented at national and international conference. These conferences were: 11th Asia-Pacific Conference on Combustion (ASPACC) and The Thirty-Seventh International Symposium on Combustion. Brief descriptions of these conference presentations are provided below.

A.1 Hydrated BA Blended with Diesel: Engine Performance.

Algayyim, Sattar Jabbar Murad, Wandel, Andrew P and Yusaf, Talal (2018) *Experimental investigation of hydrated butanol-acetone (BA) and diesel blend as alternative fuel for CI engines.* In: *37th International Symposium on Combustion*, 29 July-3 Aug 2018, Dublin, Ireland.

URL: http://www.combustionsymposia.org/2018/loadpage/pr

Abstract

A potential fuel for compression ignition engines (CI) is bio-butanol because of its beneficial physicochemical properties and ability to be produced from agriculture waste by fermentation. The feasibility of using bio-butanol from biomass is not yet clear due to its high production cost caused by low yields and expensive processes for separating it from acetone-butanol-ethanol (ABE), isopropanol-butanol-ethanol (IBE) or butanol-acetone (BA) fermentation. Instead, using intermediate fermentation products of butanol (that is ABE, IBE or BA) as a fuel has already been found to produce clean combustion. A step in producing these intermediate products is separation of water. It is therefore proposed that water-containing butanol-acetone (BA) as a fuel for CI engines could lead to extra reductions in BA production cost and could improve the combustion by reducing the temperature. An experimental investigation in a direct injection (DI) diesel engine fuelled with water-containing BA-diesel blends was carried out in this study. The effects of low-purity BA (blend of 9% vol. BA, 1% vol. water blended and 90% vol. neat diesel: BA9W1D90) on combustion, performance, and emissions characteristics were investigated at three engine speeds and full load. The results were compared with neat diesel and a 10% BA-90% diesel blend. The BA9W1D90 blend showed some improvement in brake thermal efficiency (BTE). The exhaust gas temperature (EGT), CO, UHC and NO_x emissions were significantly reduced as a consequence of including water in the test blends. Thus, water-containing BA could be a good alternative fuel for CI engines because of its production manner and reduced emissions.

A.2 ABE Blended with Diesel: Spray and Engine Performance.

Algayyim, Sattar Jabbar Murad, Wandel, Andrew P, Yusaf, Talal, Hamawand, Ihsan and Al-lwayzy, Saddam (2017) *Experimental study of spray characteristics, engine performance and emission levels of acetone-butanol-ethanol mixture-diesel blends in a diesel engine.* In: *11th Asia-Pacific Conference on Combustion*, 10-14 Dec 2017, Sydney, Australia.

URL: http://www.anz-combustioninstitute.org/ASPACC2017/

11th Asia-Pacific Conference on Combustion,
The University of Sydney, NSW Australia
10th -14th December 2017.

Experimental Study of Spray Characteristics, Engine Performance and Emission Levels of Acetone-Butanol-Ethanol Mixture-Diesel Blends in a Diesel Engine.

Sattar Jabbar Algayyim [a, b,*], **Andrew P. Wandel** [a], **Talal Yusaf** [a], **Ihsan Hamawand** [a], **Saddam Al-Wayzy** [a]

[a] School of Mechanical and Electrical Engineering, University of Southern Queensland, Toowoomba, QLD 4350, Australia.

[b] Department of Mechanical, College of Engineering, University of Al-Qadisiyah
Al-Diwaniyah, Iraq

Abstract

This paper investigates spray and engine performance of an acetone-butanol-ethanol (ABE) mixture blended with diesel fuel in a single-cylinder direct injection (DI) diesel engine**.** Spray images were evaluated using a high-speed camera under 300 bar injection pressure. Engine performance such as brake power (BP), brake-specific fuel consumption (BSFC) and in-cylinder pressure were measured. Exhaust gas emissions such as oxides of nitrogen (NO_x), carbon monoxide (CO) and unburned hydrocarbon (UHC) were also assessed. The test was carried out at three engine speeds (1400, 2000 and 2600 rpm) at full load. The experiment results showed that: liquid penetration of ABE-diesel is longer than that of diesel. BP of ABE-diesel blends was comparable with pure diesel at 2600 rpm, while the peak in-cylinder pressure was higher compared to diesel at 2000 rpm. UHC and CO emissions were significantly reduced as a result of the addition of ABE to the neat diesel, while NO_x emissions were slightly increased.

1 Introduction

With the high demand for environmental security, more attention is being paid to utilising renewable alternative fuels in diesel engines. Alcohol blends have the potential to reduce exhaust emissions as well as improve fuel efficiency due to their high oxygen content. Using alcohols as additives could also reduce dependence on fossil fuel because the alcohols are derived or produced from renewable materials such as agricultural waste. Ethanol and methanol are being widely researched in diesel engines, but some difficulties have been reported such as storage safety and low cetane number [1].

Currently, the ABE mixture has the potential to be an alternative biofuel due to its manner of production and the advantages of its properties. The volumetric ratio of ABE was 3:6:1 after fermentation processes [2-5]. Several researchers have experimentally investigated ABE blends in constant-volume chamber and diesel engines [6, 7]. These studies demonstrated that: (1) engine efficiency was improved; (2) NO*x* and soot emissions were decreased [8].

The aim of this paper is to assess the impact of ABE-diesel blends on spray characteristics, engine performance and emission levels in a DI diesel engine.

2 Methodology

2.1 Fuel Preparation and Properties

Normal butanol (B) and acetone (A) were used at 99.8% analytical grade and obtained from Chem-Supply Australia. Ethanol (E) was used at 100% analytical grade. Diesel was obtained from a local petrol station in Toowoomba, Australia as a baseline. The ABE mixture was prepared with a ratio of 3:6:1 by volume, which was used to simulate the intermediate fermentation production. Then 10% and 20% ABE was blended with diesel, referred to as 10ABE90D and 20ABE80D respectively. Miscibility and stability of the ABE-diesel blends were monitored over a one-month period before the tests were carried out on the engine. The samples were stored in glass bottles and visually observed every week, with all blends maintaining a good homogeneous mixture. Table 1 shows the properties of the separate fuel and blends.

Properties	A	E	B	D	ABE	10ABE	20ABE
Viscosity (mm^2/s) @ 40 ºC	0.35	1.08	2.22	1.9-4.1	1	2	1.8
Calorific value (MJ/kg)	29.6	26.8	33.1	42.8	31.4	41.6	40.5
Cetane number	-	8	17-25	48	-	-	-
Surface tension (mN /m)	22.6	-	24.2	23.8	-	-	-
Flash point ºC	17.8	8	35	74	-	-	-
Latent heat (MJ/kg) @ 25 ºC	518	904	582	270	595	300.4	331.2

Table 1. Fuel properties [8].

2.2 Experimental Apparatus

2.2.1 Spray Test Setup

The spray experimental test was carried out on a constant volume vessel (CVV) at atmospheric pressure. An air-driven high-pressure fuel pump was used in the fuel injection system using a solenoid Bosch-type injector with six holes (each 0.18 mm in diameter) and an injection pressure of 300 bar. A Photron Charge-Coupled Device (CCD) camera was used to capture the

---

* Corresponding author.
E-mail address: sattarjabbarmurad.algayyim@usq.edu.au

spray blends images. The camera has a resolution of 1024×1024 pixels. An LED light was used for illuminating the fuel spray to ensure constant background light for the camera. For each fuel test, the fuel tank and fuel system line were cleaned and emptied and the fuel filter was replaced with a new one. After ensuring all the injection systems were cleaned and emptied, the spray testing started with some preliminary injection tests for at least five minutes before recording the new images.

2.2.2 Engine Test Setup

The engine test was conducted using a single-cylinder, four stroke, water-cooled, DI diesel engine. An electrical dynamometer connected to the engine was used to control the load. The crank angles were measured using a crank angle encoder set up on the shaft of the engine. A Kittler 6052C pressure transducer (CT400.17) and charge amplifier connected to a data acquisition system with software (CT 400.09) were used to record cylinder pressure values at one crank angle revolution for 50 cycles each test. The exhaust gas emissions were analysed using a Coda gas analyser to measure NO_x, CO and UHC. The test was conducted at a compression ratio of 19:1 with three engine speeds (1400, 2000 and 2600 rpm) under full load. The test began at least 20 minutes before recording commenced. The experiments were carried out in triplicate to reduce the experimental error. Table 2 contains the engine specifications. Fig.1 shows operating setting of engine.

Engine model	G.U.N.T. Hamburg
Combustion type	Direct Injection Engine
Number of cylinders	1
Compression ratio	5:1-19:1
Maximum power (kW)	Approx. 6kW
Speed range (rpm)	900-3000
Bore	90mm
Stroke	74mm
Capacity	470cm^3
Maximum compression pressure	60-80 bar
Nozzle injection pressure	300 bar
Injection type	Direct Injection

Table 2. Engine specifications

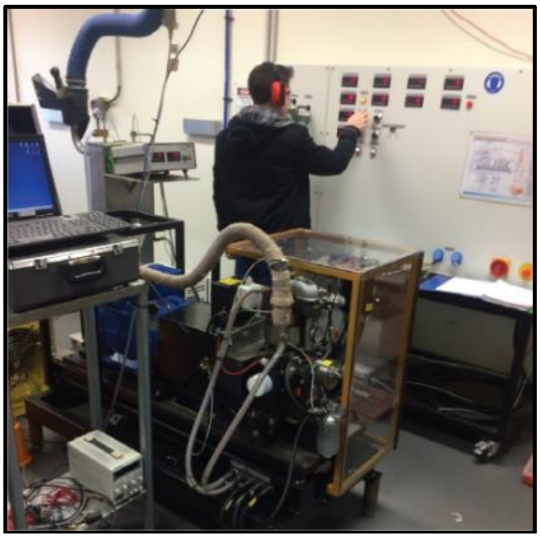


Figure 1. Operating setting of G.U.N.T engine.

3 Results and Discussion

3.1 Spray Characteristics

The macroscopic characteristics of ABE-diesel blends were obtained using a high speed- camera under various after start of injection (ASOI). Fig. 2 illustrates the spray images analysis from a Bosch type injector. Because the engine used in the experimental test was only equipped with mechanical injectors, the injection pressure used was 300 bar. Liquid spray penetration of ABE-diesel is longer than that of diesel. Fuel properties of blends have a significant impact on liquid penetration especially; under evaporating or burning conditions. According to Table 1 ABE features a much higher latent heat and lower viscosity than pure diesel, which leads to enhanced vaporisation and atomisation. Therefore the penetration length will be shorter and the plume narrower at high ambient pressure and temperature inside the diesel engine cylinder. Because almost all the physical properties change with increased ambient temperature, there is a decrease in viscosity and surface tension while there is an increase in vapour pressure. These changes significantly accelerate the atomisation and evaporation of the liquid spray.

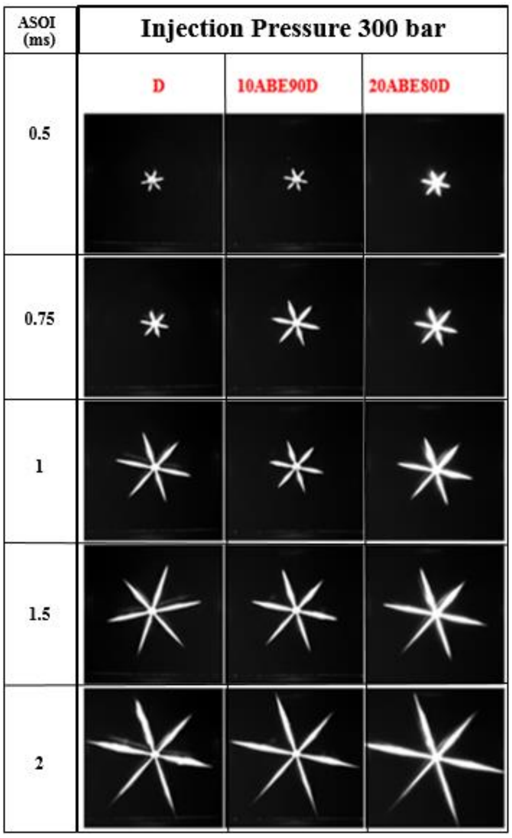


Figure 2. Spray images of test fuels.

3.2 Engine Performance

3.2.1 In-Cylinder Pressure

Figure 3 shows the relationship between the peak in-cylinder pressure trace and the crank angle of the test fuels at 1400 and 2000 rpm. 20ABE80D blend gives a maximum peak in-cylinder pressure compared to neat diesel due to the low cetane number

(CN) of the ABE blend. This results in increased ignition time and rapid in-cylinder pressure increase.

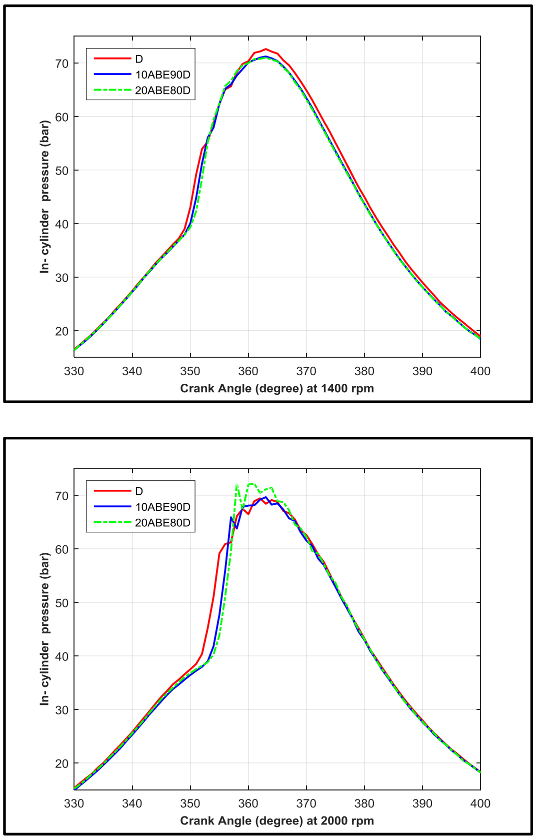
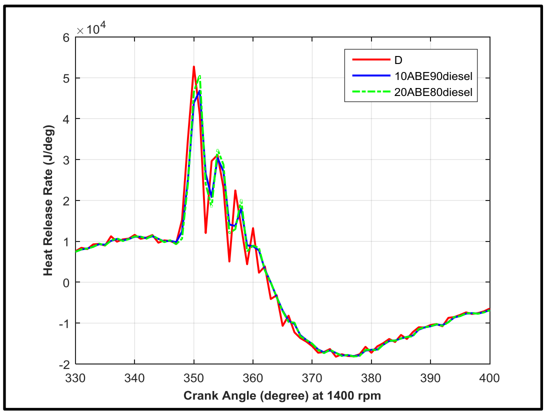


Figure 3. In-cylinder pressure at 1400 rpm and 2000 rpm.

3.2.2 Heat Release Rate (HRR)

Figure 4 presents the heat release rate of the test blends at two engine speeds. It can be seen that the diesel blend showed the highest peak HRR at the low engine speed. In contrast, the maximum HRR of 20ABE-80diesel blend occurred at 2000 rpm engine speed. The peak cylinder pressure **(**Fig. 3**)** generally corresponds to the highest HRR.



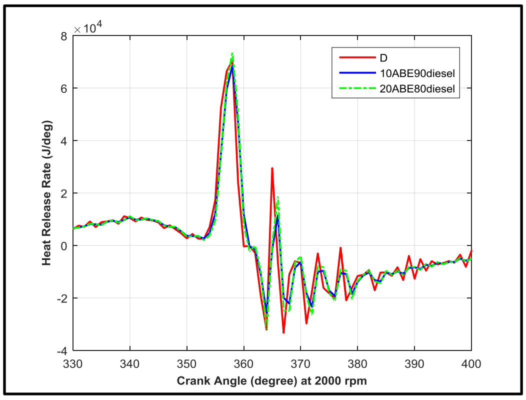


Figure 4. HRR at engine speed 1400 rpm and 2000 rpm.

3.2.3 Brake Power and Brake Specific Fuel Consumption

Figure 5 shows the variation of BP and BSFC with the engine speed of the test fuels. The BP of the ABE-diesel blend showed comparable value with diesel at the high engine speed due to its high oxygen content. BSFC was increased with both fuel blends compared to that of pure diesel due to the low calorific value of the blends (Table 1).

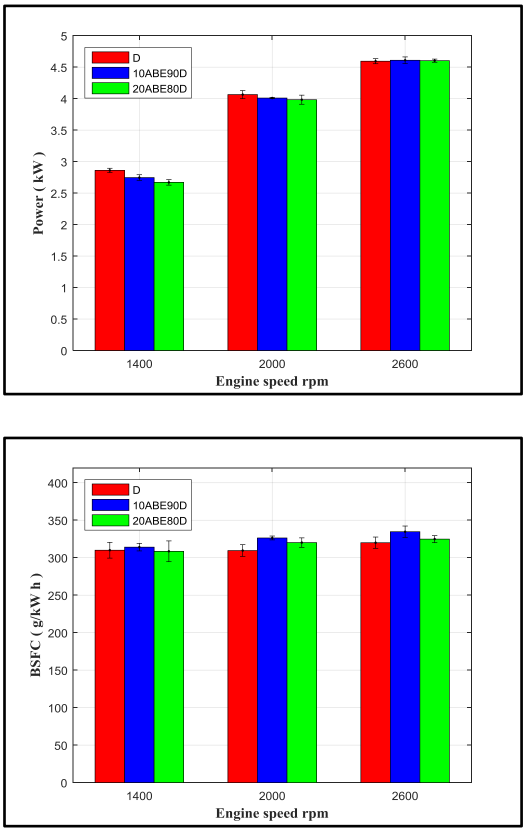


Figure 5. BP and BSFC of test fuels at three engine speeds.

3.2.4 NO_x and CO Emissions

Figure 6 presents the NO_x and CO emissions of the test fuels at various engine speeds. All ABE-diesel blends showed a slight increase in NO_x emissions at all engine speeds. CO emissions were reduced at all engine speeds. This trend could relate to: the high oxygen content and the lower cetane number of the ABE-diesel blends. These complications led to delays in ignition time and resulted in an increase in the premixed zone. This process can increase the local temperature and result in increased NO_x emissions.

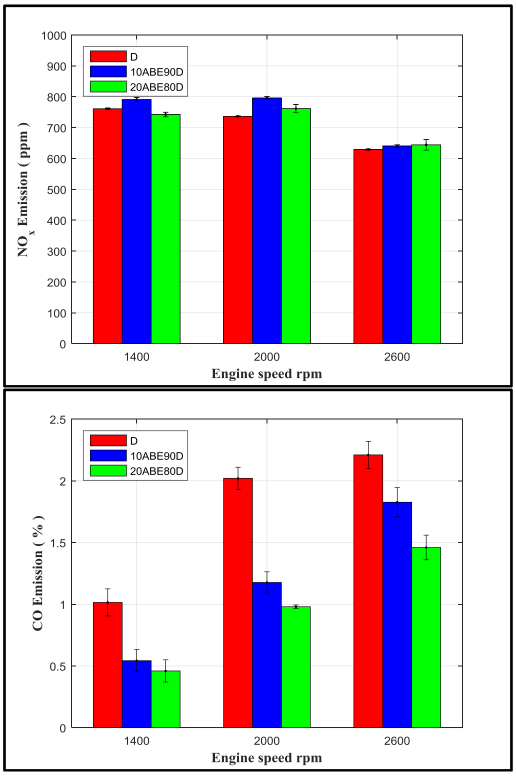


Figure 6. NO_x and CO emissions of test fuels at three engine.

3.2.5 UHC Emissions

The use of ABE-diesel blends decreased the UHC emissions compared to neat diesel at medium and high engine speeds (Fig. 7). This reduction occurred because ABE blends is a type of multi-component fuel with different volatilities, which might produce micro-explosions and thus promote combustion performance. Also, the difference in droplet lifetime between ABE (3.25 s/mm^2) and neat diesel (3.75 s/mm^2) at 823 K affects the reaction time of ABE blends, which results in increased mixing time and leads to complete reaction resulting in decreased UHC emissions [9].

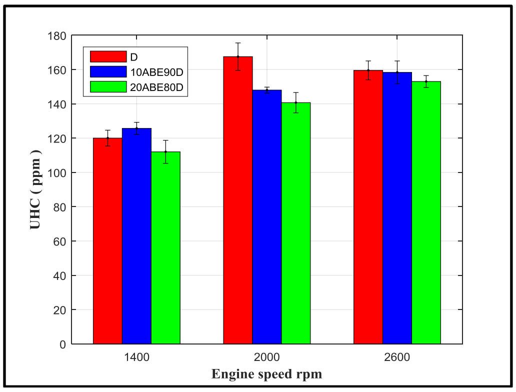


Figure 7. UHC emission of test fuels at three engine speeds.

4 Conclusions

The experimental work has concluded some significant results for the test fuels. The results are as follows:

- Liquid spray penetration of ABE-diesel blend is longer than that of diesel at ambient conditions.
- The BP of the ABE-diesel blends was comparable with neat diesel at the high engine speed, while the peak in-cylinder pressure and HRR were higher compared to diesel at the medium engine speed.
- UHC and CO emissions were significantly reduced as a result of the addition of ABE to diesel blends, while NO_x emissions were slightly increased.

5 Acknowledgments

The first author thanks the Iraqi Government Ministry of Higher Education and Scientific Research. The authors are also grateful to (USQ staff) for assisting with experiments.

References

[1] Shahir, S. A., Masjuki, H. H., Kalam, M. A., Imran, A., and Ashraful, A. M., RENEW SUST ENERG REV 48 (2015) 62-78.

[2] Abd-Alla, M. H., Zohri, A. N., El-Enany, A. W., and Ali, S. M., ANAEROBE 32 (2015) 77-86.

[3] Bellido, C., Infante, C., Coca, M., González-Benito, G., Lucas, S., and García-Cubero, M. T., BIORESOURCE TECHNOL 190 (2015) 332-338.

[4] Cai, D., Zhang, T., Zheng, J., Chang, Z., Wang, Z., Qin, P.-y, and Tan, T.-w., BIORESOURCE TECHNOL 145 (2013) 97-102.

[5] Li, H.-g., Ofosu, F. K., Li, K.-t., Gu, Q.-y., Wang, Q., and Yu, X.-b., BIORESOURCE TECHNOL 172 (2014) 276-282.

[6] Wu, H., Nithyanandan, K., Lee, T. H., Lee, C.-f. F., and Zhang, C., ENERG FUEL 28 (10) (2014) 6380-6391.

[7] Wu, H., Nithyanandan, K., Zhang, J., Lin, Y., Lee, T. H., Lee, C., and Zhang, C., APPL ENERG 149 (2015) 367-378.

[8] Wu, H., Nithyanandan, K., Zhou, N., Lee, T. H., Lee, C.-f. F., and Zhang, C., FUEL 142 (2015) 109-116.

[9] Ma, X., Zhang, F., Han, K., Yang, B., and Song, G., FUEL 160 (2015) 43-49.

Appendix B: Heat Release Rate

B.1

The Heat Release Rate (HRR) is calculated without accounting for cylinder wall heat losses:

$$\frac{dQ}{d\varphi} = \frac{\gamma}{\gamma - 1} P \frac{dV}{d\varphi} + \frac{1}{\gamma - 1} V \frac{dP}{d\varphi} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots . (B.1)$$

where Q is the heat energy value, φ is the crank angle, P is the in-cylinder pressure, V is the volume of the gas inside the engine cylinder and γ = 1.35 is the specific heat ratio. When applied to engine measurements, Equation (B.1) provides the Apparent Heat Release Rate.

The cylinder volume V at any crank position φ is:

$$\mathrm{V} = V_c + \boldsymbol{\frac{\pi B}{4}(l + a - s)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(B.2)}$$

where V_c = clearance volume, s is the distance between the crank axis and the piston pin axis and is given by

$$s = a \cos \varphi + (l^2 - a^2 (\sin \varphi)^2\ )^{½} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(B.3)}$$

Here, θ is the crank angle. Equation (B.1) can be rearranged and differentiated to yield the rate of change of cylinder volume with respect to crank angle (θ):

$$\boldsymbol{\frac{dv}{d\varphi} = \left(\frac{\pi A}{180}\right) \times a \left[(\sin\left(\frac{\pi\varphi}{180}\right) + \left[\frac{R^2 sin^2\left(\frac{\pi\varphi}{180}\right)}{\left[(2\times\sqrt{1 - R^2 sin^2\left(\frac{\pi\varphi}{180}\right)}\right]}\right]\right]} \dots\dots\dots\dots\dots\dots\dots\dots \text{(B.4)}$$

Here, R = $\boldsymbol{\frac{l}{a}}$, R = ratio of connecting rod length to crank radius.

A = $\frac{\pi B^2}{4}$, $\boldsymbol{l}$ = connecting rod length, a = crank radius, B = cylinder bore,