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INYUVESI YAKWAZULU-NATALI

PRODUCTION, EVALUATION AND TESTING OF BIOETHANOL FROM *MATOOKE* PEELS SPECIES AS AN ALTERNATIVE FUEL FOR SPARK-IGNITION ENGINE: A CASE STUDY OF UGANDA

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Supervisor's Declaration

As the candidate's supervisor, I agree/~~do not agree~~ to the submission of this thesis.

27th February 2020

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Declaration 2 - Publications

This section presents the articles that form part and/or include the research presented in this thesis. The following papers have been published:

Publication 1

Yusuf, A. A., & Inambao, F. L. (2019). Bioethanol Production Techniques from Lignocellulosic Biomass as Alternative Fuel: A Review. *International Journal of Mechanical Engineering and Technology*, 10(6), 34-71. **IAEME Publications**
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Publication 2

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Yusuf, A. A., & Inambao, F. L. (2019). Effect of Cold Start Emissions from Gasoline-Fueled Engines of Light-Duty Vehicles at Low and High Ambient Temperatures: Recent Trends. *Case Studies in Thermal Engineering.* 14, 100417. http://doi.org/10.1016/j.csite.2019.100417. **Elsevier B.V.**
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Publication 4

Yusuf, A. A., & Inambao, F. L. (2020). Characterization of Ugandan Biomass Wastes as the Potential Candidates Towards Bio-Energy Production. *Renewable and Sustainable Energy Reviews.* 117, 109477. http://doi.org/10/1016/j.rser.2019.109477. **Elsevier B.V.**
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Publication 5

Yusuf, A. A., Inambao F. L., Sharif N. S., Shu'ibu A. H., & Karthickeyan V. (2019). Comparative Study on Pyrolysis and Combustion Behavior of Untreated *Matooke* Biomass Wastes in East Africa via TGA, SEM, and EDXS. *International Journal of Energy and Environmental Engineering.* pp.1-9. doi.org/10.1007/s40095-019-00331-2. **Springer Nature.**
Status: (Published)

Publication 6

Yusuf, A. A., & Inambao, F. L. (2018). Bioethanol Production from Different *Matooke* Peels Species: A Surprising Source for Alternative Fuel. *Case Studies in Thermal Engineering.* 13, 100357. http://doi.org/10.1016/j.csite.2018.11.008. **Elsevier B.V.**
Status: (Published)

Publication 7

Yusuf, A. A., & Inambao, F. L. (2019). Effect of Low Bioethanol Fraction on Emissions, Performance and Combustion Behavior in a Modernized Electronic Fuel Injection Engine. *Biomass Conversion and Biorefinery.* http://doi.org/10.1007/s13399-019-00519-w. **Springer Nature.**
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Abstract

Conversion of new lignocellulose biomass (LCB) waste to energy is an innovative technique for waste valorization and management which reduces environmental pollutions and offers socioeconomic benefits. This has made the LCB to be significant due to its novel behavior towards bioenergy. The aims of this study is to characterize the biomass, evaluate and produce the bioethanol fuels from unique LCB which is *matooke* peels species, and examined the emissions and combustion effects of low content rates of bioethanol blends with gasoline in a modernized spark-ignition engine.

The *matooke* peels species such as *Mbwazirume* and *Nakyinyika* biomass peels, which are pretreated and untreated were characterized to identify its use in bioenergy production. This characterization of biomass was carried out using various analyses such as proximate and ultimate analysis, thermo-gravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), atomic absorption spectroscopy (AAS), scanning electron microscopy (SEM), and energy dispersive X-ray spectrometer (EDXS). Experimental findings reveal that the pretreated *Mbwazirume* biomass exhibits excellent solid fuel properties when compared to untreated *Mbwazirume*, pretreated and untreated *Nakyinyika* biomass peels.

Bioethanol fuels were produced from *Mbwazirume* and *Nakyinyika* biomass peels through a fermentation process using *Saccharomyces cerevisiae* and analyzed using ANOVA. The study also optimized production variables and determined the models for separate hydrolysis and fermentation (SHF). The properties of the bioethanol were measured according to relevant ASTM standards and compared with the standard ethanol and gasoline. *Mbwazirume* biomass shows higher bioethanol yields and excellent fuel properties, this serve as a fuel of choice for further experiment.

The bioethanol ratios were blend with gasoline at (E0, E5, E10, and E15) used in the development of further experiments on engine and combustion performance, and exhaust emissions test in a modernized TD201 four-stroke petrol engine. The results obtained were computed, modeled, evaluated and analyzed. Results show that the small differences in properties between bioethanol-gasoline blends are enough to create a significant change in the combustion system. These effects lead to behavioral mechanisms which are not easy to analyze or understand, sometimes make it difficult to identify the fundamentals of how blend ratios affect emissions and performance.

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Chapter 1: Introduction

1.1 Background

Biofuels, derived from biomass, include liquid, solid, and gas fuels, such as wood pellets, ethanol, biodiesel, and biogas, which are used to deliver renewable energy services in the form of heating and cooling, transportation, and electricity. For transportation, liquid biofuels are seen as the preferred route to easily replace current liquid petroleum fuels, since this incurs relatively little additional infrastructure cost, and offers a direct path to decarbonize the transport system [1]. The global dependency on fossil fuels for energy generation has significant implications for the environment, of which global climate change due to carbon dioxide (CO_2) emissions are among the most serious [2]. These challenges have led to new approaches focusing on energy consumption management and alternative fuel sources which are urgently needed in order to meet energy demands, increase efficiency, and reduce greenhouse gas (GHG) emissions [3].

There is significant potential for agricultural involvement in the production and consumption of biomass energy. For instance, Uganda is ranked the second largest producer of bananas at 11.1 m tons per year, and the number one consumer of bananas at 240 kg per capita per annum [4]. This means that bananas are a key part of many families' everyday diet, which in return generates considerable quantities of banana peels each day all year round [5]. There are different types of bananas grown in Uganda for food consumption. These have been classified as green bananas (*Matooke*), plantain, and yellow or sweet bananas [6]. *Matooke* (*Musa-AAA-EA*) is a variety of banana indigenous to Uganda and is the most essential staple food crop for human consumption. It comes from the family of bananas known as East African highland bananas. It appears to be green in color and thick at the midsection [7] which is different from yellow bananas, and cannot be peeled in the same way as yellow bananas.

Some of these peels are used as animal feed or as local briquettes but nevertheless about 61.8 kg per capita per annum of *Matooke* peels produced in Uganda become waste, due to the lack of sufficient structure and indiscriminate dumping. This huge amount of waste leads to environmental health problems, and releases GHG. However, this waste is a lignocellulosic biomass (LCB) which can be utilized as a readily available and renewable low-cost raw material for biofuel production due to its high starch content (~70 wt.%) [8,9]. Among the various biofuels, bioethanol presents the most suitable renewable, bio-based and eco-friendly fuel for spark-ignition (SI) engines mainly because it has similar properties to gasoline in terms

of high octane number, high flame speed, low stoichiometric air-fuel ratio and low heating value [10–12].

Utilizing these new LCBs for alternative fuel can reduce the use of fossil fuels, increase engine efficiency and minimize CO_2, NOx and SOx emissions released into the atmosphere as a result of fossil fuel combustion. Though some researchers have carried out studies on various biomass bioethanol in SI engines, there is no published literature available on bioethanol for use in SI engines derived from *matooke* peel biomass, and its characterization (such as TGA, FT-IR, AAS, and SEM-EDS). Besides, most researchers concentrate on how to replace gasoline with alternatives without considering the effects of those alternatives on the engine. Thus, this research aimed to characterize the biomass, evaluate and produce bioethanol fuel from a unique LCB which is the peel of the *matooke* species, and examined the emissions and combustion effects on low content rates of bioethanol blends with gasoline in a modernized spark-ignition engine.

1.2 Statement of the problem

The increase in demand for and identification of the resources for energy are key issues for most countries in Africa. For instance, in Uganda, electricity distribution is one of the lowest in Africa; estimated at only 22 % of the total Ugandan population and dropping to 8 % to10 % in rural areas. Furthermore, the country is highly vulnerable to oil price shocks as it imports almost all of its 31 490 barrels per day (5 006.5 m^3/d) of oil from Kenya. These makes the energy consumption from transportation sector. Such limited and unreliable energy access represents the underutilization of the large amount of biomass (*Matooke* peels) waste available which can be a renewable and sustainable source for bioenergy production. *Matooke* peels, which are different from sweet banana peels, is a key part of many families' everyday diet. About 61.8 kg per capita per annum of *Matooke* waste is produced, posing considerable disposal problems and ultimately leading to environmental pollution. These challenges have practical and policy implications in Uganda related to energy consumption management and alternative sources for biofuel which are now an urgent necessity in order to meet energy demands, increase efficiency, and reduce GHG emissions. This waste can be utilized as a readily available and renewable low-cost raw material for bioethanol production. Finding an alternative use for this biomass waste by converting it to biofuels will go a long way in addressing poverty by providing employment.

1.3 Main objective of the study

The main purpose of this research was to produce, evaluate and test the bioethanol from *matooke* peels species waste as blend fuels in an SI engine.

1.4 Specific objectives of the study

The specific objectives of the study were:

1. To characterize the *matooke* peels species suitable for bioethanol production.
2. To synthesize bioethanol from selected *matooke* species under several conditions.
3. To determine and optimize various effects of process parameters for enhancing the quality of bioethanol extracted from *matooke* peels.
4. To conduct engine performance and emission characteristics tests of bioethanol blend fuels.

1.5 Significance of the research

A huge amount of *matooke* peels produced in Uganda becomes waste due to the lack of sufficient structure and indiscriminate dumping. This has led to research and the development of bioethanol through using waste that does not compete with the food chain, which is sustainable and efficient regarding both costs and energy. As reported in the literature, bioethanol has similar properties to gasoline in terms of high-octane number, high flame speed, low stoichiometric air-fuel ratio and low heating value. It is suggested that the current research on *matooke* peels can be added to the biomass database for future bioenergy production. In addition, this will help in identifying the opportunities for reaching Uganda's bioenergy targets over the medium to long term, since bioenergy can be used for many purposes such as generating electricity as well as transportation fuel. Now that liquid fuel extracted from *matooke* peels has been tested and evaluated in a SI engine, government and development agencies can support the research for small-scale bioethanol production, which can then help to provide clean, accessible energy that is vital for rural development, poverty alleviation, and will provide an additional source of income for the government.

1.6 Layout of the thesis

Chapter 1 presents an overview of the research work by explaining the background of the study, aims and objectives, and the significance of the research.

Chapter 2 reviews the potential techniques of bioethanol production from different lignocellulosic biomass as alternative fuel.

Chapter 3 highlights the progress in bioethanol-gasoline blends and their effects on the performance, emissions and some combustion characteristics in SI engines under different operating conditions.

Chapter 4 surveys the recent trends in cold-start emission behavior regarding the impact of changes in ambient temperature in relation to the advanced technology of gasoline direct injection (GDI) and port fuel injection (PFI) vehicles. It also presents the influence of lower combustion temperature and rich air/fuel mixture at very low temperature conditions.

Chapter 5 reports the characterization of the new LCB material such as pretreated *Mbwazirume* peel (MP) and *Nakyinyika* peel (NP) biomass using various analyses such as proximate and ultimate, TGA, FT-IR, AAS, and SEM-EDS. This was in order to assess their suitability for bioenergy application in Uganda.

Chapter 6 characterizes the unique biomass from the variety of *Matooke* peel which is untreated *Mbwazirume* waste peel (UM-WP) and untreated *Nakyinyika* waste peel (UN-WP). It is suggested that this exploration can be added to the biomass database as an alternative energy source.

Chapter 7 investigates the feasibility of producing bioethanol fuel from a renewable and sustainable energy resource which is *matooke* species peels through a fermentation process using *Saccharomyces cerevisiae*. The properties of the bioethanol were measured according to relevant ASTM standards and compared and analyzed by gas chromatography. These bioethanol properties are within the acceptable range of standard ethanol and gasoline.

Chapter 8 examines the effects of low content rates of *Mbwazirume* bioethanol-gasoline blends (E0, E5, E10, and E15) in a modernized TD201 four-stroke petrol engine, equipped with efficient electronic fuel injection (EFI) systems. These blend fuels were tested under various engine speeds in order to assess engine emissions, performance, and combustion characteristics because ignition timing is also an alternative process to predict engine performance.

Chapter 9 presents conclusions and recommendations for future work.

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Chapter 2: Paper 1

Bioethanol Production Techniques from Lignocellulosic Biomass as Alternative Fuel: A Review

This chapter critically reviews the potential techniques of bioethanol production from different lignocellulosic biomass as alternative fuel. The article has been published in the *International Journal of Mechanical Engineering and Technology*, IAEME Publications.

BIOETHANOL PRODUCTION TECHNIQUES FROM LIGNOCELLULOSIC BIOMASS AS ALTERNATIVE FUEL: A REVIEW

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ABSTRACT

Bioethanol production from lignocellulosic biomass (LCB) has been demonstrated as alternative to conventional fuel, as it is considered to be renewable and clean energy. The major problem of bioethanol is the availability of biomass materials for its production. This review paper aims to provide an overview of the recent developments and potential regarding production techniques, ethanol yields, and properties, as well as the effects of bioethanol fuel as replacement for fossil fuel. The literature indicates that the best results have been obtained with cellulase and β-glucanase cocktail which significantly increases bioethanol production compared to fermented acid pretreatment. The classification of pretreatment, hydrolysis, and fermentation have significant effects on physico-chemical properties of bioethanol fuel, which also influence the internal combustion engines. Difference in operating conditions and physico-chemical properties of bioethanol fuels, may change the combustion behaviors and sometimes makes it difficult to analyze the fundamentals of how it affects emissions.

Keywords: Bioethanol; lignocellulosic biomass; combustion behaviors; emissions.

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1. INTRODUCTION

Energy consumption associated with the transportation sector has contributed to a world problem. The world's energy demand is increasing every day and the problem of fossil fuel depletion is looming (Iodice & Senatore, 2016). These challenges have led to new approaches focusing on energy consumption management and alternative fuel sources so as to increase efficiency and reduce greenhouse gas emissions respectively (Yusuf & Inambao, 2018). Biomass is the most common form of a renewable primary energy resource that can provide alternative transportation fuels (McKendry, 2002; Sun & Cheng, 2002). Biofuels are a variety of fuels which can be produced from agro-industrial waste, algae material or various

lignocellulosic biomass (LCB) sources in many different ways (Calam, Içingür, Solmaz, & Yamk, 2015). Among the various biofuels, bioethanol presents the most suitable renewable, bio-based and eco-friendly fuel for SI engines mainly because it has similar properties to gasoline in terms of high octane number, high flame speed, low stoichiometric air-fuel ratio and low heating value (Calam et al., 2015; Iliev, 2015; Zhen, 2018).

Thus, production of bioethanol from biomass is a process of decreasing the consumption of crude oil and reduce CO_2, NOx and SOx emissions released into the atmosphere as a result of fossil fuel combustion (Thangavel, Momula, Gosala, & Asvathanarayanan, 2016; Tibaquir & Huertas, 2018). Many researches have been conducted on production of bioethanol from a simple conversion of various biomass sources such as sugarcane, corn, cassava, banana peels, rice straw and other agricultural waste by means of fermentation (P. Kumar, Barrett, Delwiche, & Stroeve, 2009; Xu & Huang, 2014), to the multi-stage conversion system of LCB into bioethanol (Binod et al., 2010; Sarkar, Ghosh, Bannerjee, & Aikat, 2012). In this context, the utilization of various agricultural residues (such as wheat straw, rice straw, banana peel, sugarcane bagasse, rape straw, and corn stover) containing carbohydrates for the production of bioethanol have been reported. In Uganda, 91.4 kg per capita of *Matooke* (banana) peels are generated per year, a small portion of which is used for animal feeds, and briquettes while a large portion is left to waste away contributing to an increase in environmental residues. It is important to research the possible ways of adding value to these wastes, but production costs can vary widely considering conversion process, the scale of production, lignocellulosic material and region. The current research focused on the development of bioethanol through agro-industry waste that does not compete with the food chain, which is sustainable and efficient regarding both costs and energy. This review paper aims to give an overview of the recent studies on production techniques, ethanol yield, properties, and useful characteristics of bioethanol from LCB as replacement for fossil fuel. This will provide a benchmark for the development of biofuels from *Matooke* peels in Uganda.

2. LIGNOCELLULOSIC BIOMASS COMPOSITION AND STRUCTURE

LCB is an abundant, renewable source of carbohydrates for microbial conversion to chemicals and fuels (Geddes, Nieves, & Ingram, 2011). It is derived from agricultural residues, such as straw, wood and other agricultural waste (Aditiya et al., 2016; Domínguez-Bocanegra, Torres-Muñoz, & López, 2015). This type of biomass can be converted into liquid fuel. This in turn improves the CO_2 balance, and since it is a waste resource, it does not compete with human food chain (Soccol et al., 2010). The composition of LCB is categorized into three main parts: cellulose (30 % to 50 % dry wt.), hemicellulose (20 % to 40 % dry wt.) and lignin (10 % to 20 % dry wt.) (Limayem & Ricke, 2012; Putro et al., 2015; Sebayang et al., 2016). The molecular structure of cellulose, hemicellulose, and lignin are shown in Fig. 1.
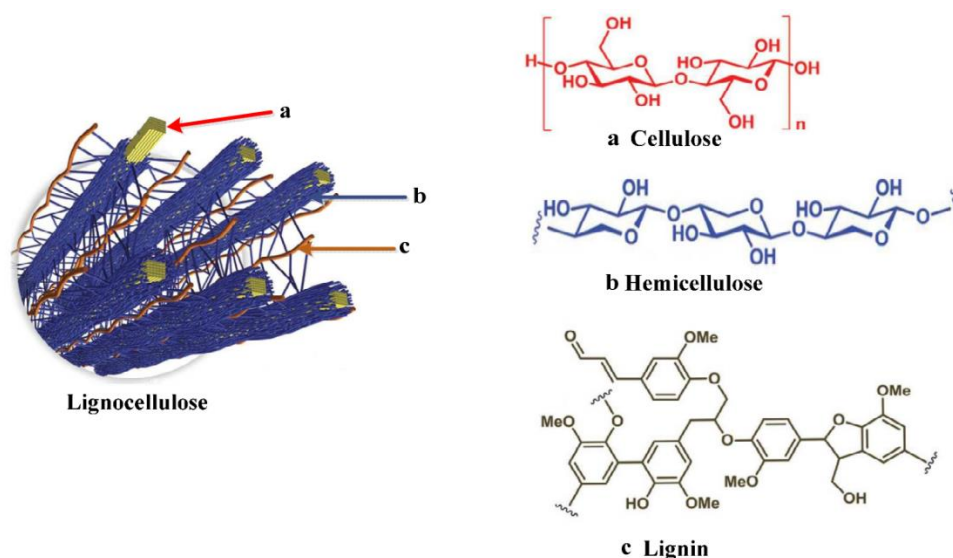
Figure 1 Lignocellulosic biomass (a) Cellulose; (b) Hemicellulose; (c) Lignin (Brandt, Gräsvik, Hallett, & Welton, 2013; Kobayashi & Fukuoka, 2013).

2.1. Cellulose

Cellulose (C6H10O5)n is a hexoses sugar from agricultural biomass and woody (Balat, 2011). It is a linear polymer of glucose monomers (D-glucose) linked to β-(1,4)-glycosidic bonds, and consists of a long chain of β-glucose monomers gathered into micro-fibril bundles (Ebringerová & Thomas, 2005; Haghighi Mood et al., 2013). Cellulose is insoluble in water, and allow the hydrolysis process to break down the polysaccharide to free sugar molecules by increasing water content known as saccharification (Hamelinck, Van Hooijdonk, & Faaij, 2005). Figures 2, 3 and 4 describe the schematic concepts of a biorefinery from LCB sources as the starting point for the production of a variety of molecules, and their application for fuels and biochemical platforms related to the agro-industry. Chemicals that can serve as a starting point for other chemicals are often called platform chemicals (Engdahl & Tufvesson, 2012).

The overall hydrolysis of cellulose produces only glucose, which can be converted into different forms of biochemical substances and chemical (Fig. 2). Biological processes can lead to a wide range of substances such as bioethanol, organic acids, glycerol, sorbitol, mannitol, fructose, enzymes, and biopolymers. This is due to the existence of an exclusive and common metabolic pathway for the great majority of living beings (Päivi Mäki-Arvela, Salmi, Holmbom, Willför, & Murzin, 2011a; Pereira, Couto, & Anna, 2008). Chemical or enzymatic processes can be converted into hydroxymethylfurfural (HMF) which is an important intermediate platform for the production of dimethylfuran (DMF) or furan-based polymers (Pereira et al., 2008).

Figure 2 Schematic concepts of biorefinery from lignocellulosic biomass composition (cellulose products) (Pereira et al., 2008).

2.2. Hemicellulose

Hemicellulose $(C_5H_8O_4)_n$ is a short, highly branched polymer of pentose sugars (D-xylose and L-arabinose) and hexose (D-glucose, D-mannose and D-galactose) (Kuhad, Gupta, Khasa, Singh, & Zhang, 2011). Hemicelluloses are associated to cellulose as large source of carbon in plants and xyloglucans or xylans depending on the types of plants (Bioprocessing, Fuels, & Energy, 1994). The presiding sources of hemicelluloses biomass are woody, softwoods, and hardwoods (Limayem & Ricke, 2012). Hemicellulose is more readily hydrolyzed compared to cellulose because of its branched, amorphous nature.

Xylose can be hydrogenated to produce xylitol, which can be used as a non-carcinogenic sweetener, with the same sweetening power of sucrose and with metabolization in the humans independent of insulin. Xylose can be biologically converted to single cell proteins (SCP) and to a variety of fuels and solvents, such as bioethanol by yeasts with the ability to ferment pentose (Pichia stipitis, Candida sheratae) (Pereira et al., 2008). Xylitol, by microorganisms with exclusively nicotinamide adenine dinucleotide phosphate (NADPH) dependent reductase activities on xylose (Vásquez, De Souza, & Pereira, 2006); biopolymers (polyhydroxyalkanoates, polylactate etc); a series of organic acids (succinic, propionic, acetic, lactic and butyric); solvents (butanol and acetone) and other fuels or fuel additives (DMF, butanol, 2,3 butanediol) (Clark & Deswarte, 2015) (Fig. 3).
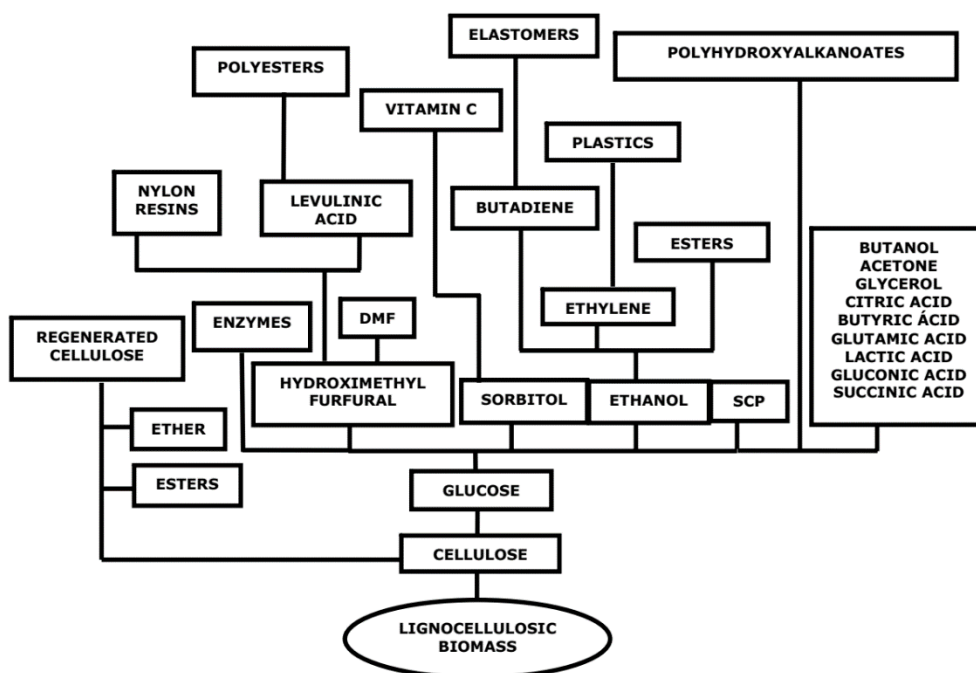
Figure 3 Schematic concepts of biorefinery from lignocellulosic biomass composition (hemicellulose products) (Pereira et al., 2008).

2.3. Lignin

Lignin $[C_9H_{10}O_3 (OCH_3)_{0.9-1.7}]_n$ is an organic compound from three different monomers (coniferyl, synapyl alcohols, and p-coumaryl) joined together by a set of linkages to create a matrix (Sánchez, 2009). This matrix consist of various functional groups, such as methoxyl, hydroxyl, and carbonyl, which shows a high polarity to the lignin macromolecule (Feldman, Banu, Natansohn, & Wang, 1991). Lignin is among the obstacles to fermentation of LCB, which makes it unaffected by chemical and biological degradation, but affects the quality of bioethanol production (Taherzadeh & Karimi, 2008).

Lignin offers useful opportunities to obtain high-value products, such as carbon fibers, emulsifiers, dispersants, sequestrants, surfactants, binders and aromatics (Rosas, Berenguer, Valero-Romero, RodrÃguez-Mirasol, & Cordero, 2014). The application of lignin is in the pulp and paper industry, which serve as a biofuel to replace fossil fuels for transportation, and the lignin-depleted black liquor can be reused in the cooking operation (Pereira et al., 2008) (Fig. 4).
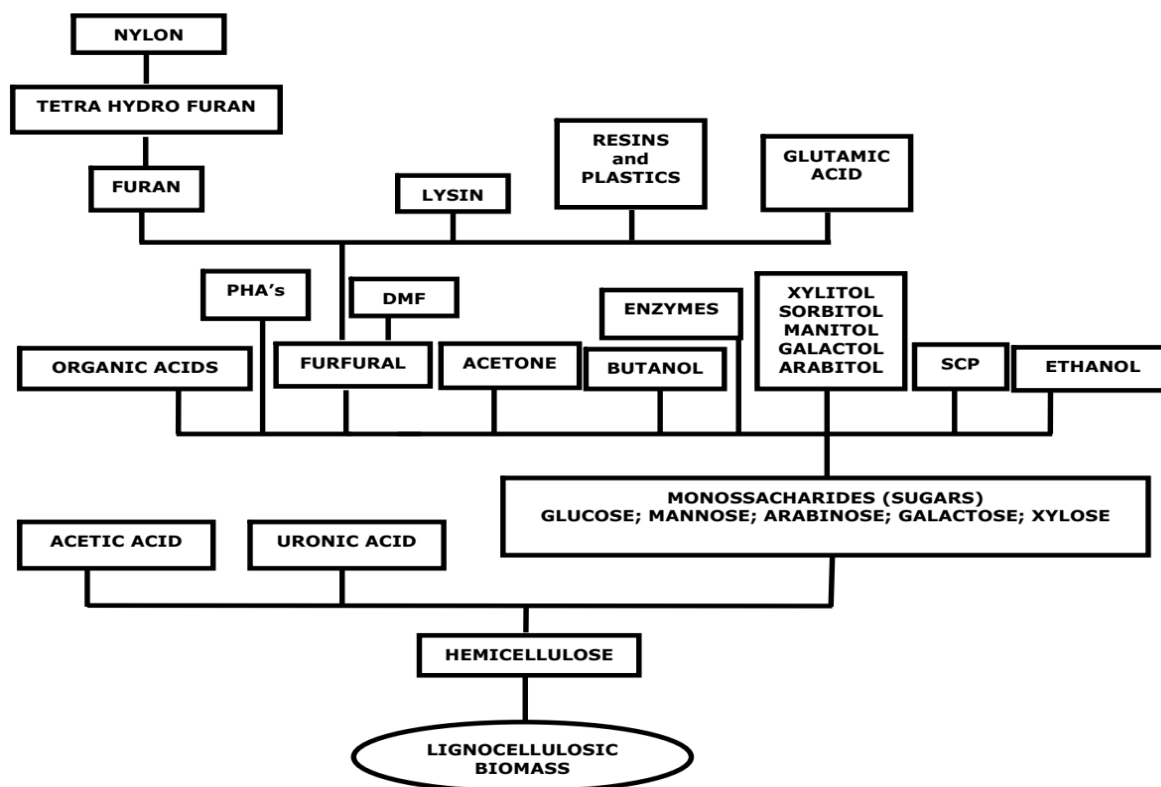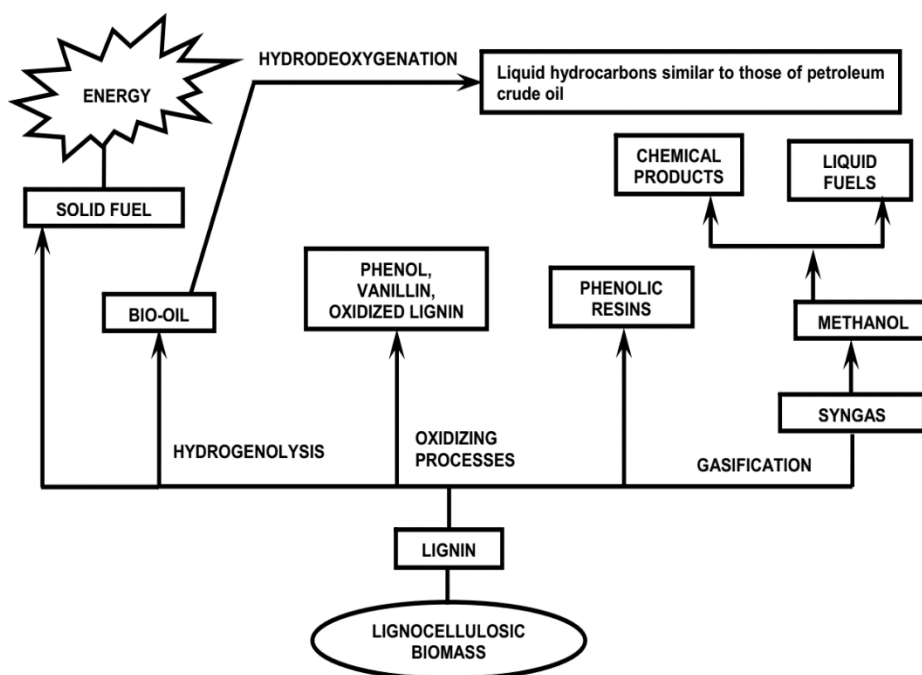
Figure 4 Schematic concepts of biorefinery from lignocellulosic biomass composition (lignin products) (Pereira et al., 2008).

3. PROCESS OF CONVERTING LIGNOCELLULOSIC BIOMASS TO BIOETHANOL

The conversion process of ethanol depends on the types of LCB used. Generally, bioethanol production from LCB comprises different stages: (1) pretreatment (2) hydrolysis of cellulose and hemicellulose (3) sugar fermentation and (4) distillation and purification of the ethanol to meet fuel specifications (Bon & Ferrara, 2010; Demirbaş, 2005).

3.1. Pretreatment technologies

This process has an essential effect on the overall process of bioethanol from LCB, which makes the cellulose accessible to hydrolysis for conversion to ethanol fuels (Srichuwong et al., 2009). Various pretreatment techniques change the properties and structure of the LCB, and improve the rate hydrolysis (P. Kumar et al., 2009). Pretreatment technologies are divided into four categories: (1) physical (Keikhosro Karimi & Taherzadeh, 2016) (2) physico-chemical (Bonner et al., 2016) (3) chemical (Williams, Crowe, Ong, & Hodge, 2017) and (4) biological pretreatment (Amin et al., 2017). The advantages and disadvantages of the pretreatment processes for LCB materials are summarized in Table 1.

3.1.1. Physical pretreatment

Physical pretreatment is a process of reducing the particle size of the feedstock to increase the surface or volume ratio, which eases the subsequent processes in the production (Harmsen, Huijgen, López, & Bakker, 2010). Saccharification produces fermentable sugars from cellulosic materials via enzymatic degradation, acidic, and ionic hydrolysis (C. Zhao et al., 2018). The types of physical pretreatment appear below.

3.1.1.1. Mechanical

Mechanical pretreatment of LCB is an important step for improving the bioconversion potential through particle densification and distribution, enzymatic accessibility, and the overall

transformation of lignocellulosic material into biofuels without the generation of toxic side streams (Barakat et al., 2014). This process involves the breakdown of LCB through a combination of chipping, grinding, or milling which reduces cellulose crystallinity (Cheng & Timilsina, 2011). It can be considered environmentally friendly because it does not require additional chemicals (Inoue, Yano, Endo, Sakaki, & Sawayama, 2008), and thus inhibitors are not generated (Da Silva, Inoue, Endo, Yano, & Bon, 2010). The pretreatment process generates new surface area, improves flow properties, and increases the bulk density and porosity (Amin et al., 2017). The size of the materials is usually 10 mm to 30 mm after chipping and 0.2 mm to 2 mm after milling or grinding (Sun & Cheng, 2002). The energy requirements are dependent on the final particle size and reduction in crystallinity of the lignocellulosic material (Brodeur et al., 2011). Zheng et al. (2009) reported that mechanical processes such as attrition milling, ball milling, and compression milling treatment could be used to destruct lignin and give better access for enzymes to attack cellulose and hemicellulose in enzymatic hydrolysis.

3.1.2. Physico-chemical pretreatment

3.1.2.1. Steam explosion (auto-hydrolysis)

Steam explosion is the most commonly used method for the pretreatment of lignocellulosic materials (Balat, 2011). It is also considered the most cost-effective option for hardwood and agriculture residues (Prasad, Singh, & Joshi, 2007) but is less effective for softwood (Saini, Saini, & Tewari, 2015) because of the low content of acetyl groups in the hemicellulosic portion of softwoods (Sun & Cheng, 2002). In this method, LCB is exposed to high-pressure saturated steam at a temperature of 160 °C to 260 °C and a corresponding pressure of 5 atm to 50 atm for a few minutes (Heerah, Mudhoo, Mohee, & Sharma, 2008). The gradual release of pressure, and the steam swell in a lignocellulosic matrix, causing individual fibers to separate and the cell wall structure to be disrupted (Agbor, Cicek, Sparling, Berlin, & Levin, 2011). Acid can be added as a catalyst during steam explosion, but addition of acid is not mandatory. Steam pretreatment is termed auto-hydrolysis if no exogenous acid catalyst is added to the plant biomass (Amin et al., 2017). The increase in SO_2 or sulfuric acid (H_2SO_4) has been proposed as one of the most effective pretreatment methods for softwood material, but it has some disadvantages (Berlin et al., 2006; L. Kumar, Arantes, Chandra, & Saddler, 2012).

3.1.2.2. Ammonia fiber explosion (AFEX)

This process utilizes ammonia to decrease crystallinity of cellulose in lignocellulosic biomass, as well as to disrupt carbohydrate lignin bonds (Maurya, Singla, & Negi, 2015). In this process, liquid ammonia is added to the biomass under moderate pressure (100 psi to 400 psi) and temperature (70 °C to 200 °C) before rapidly releasing the pressure. The main process parameters are the temperature of the reaction, residence time, ammonia loading, and water loading (Bals, Rogers, Jin, Balan, & Dale, 2010). Ammonia fiber explosion pretreatment increases the lignocellulosic digestibility and enhances the yield from the enzymatic hydrolysis as the subsequent process (Taherzadeh & Karimi, 2008). Research by (R. Kumar, Mago, Balan, & Wyman, 2009) reported that the ammonia fiber explosion method shows no inhibition of the subsequent processes in the production line, and cell walls extractives, for instance lignin phenolic fragments, remain on the surface of cellulose. Alizadeh et al. (2005) pretreated switchgrass (*Panicum virgatum*) using ammonia fiber explosion at 100 ºC with ammonia to biomass ratio of 1:1, yielding 0.2 g ethanol/g dry biomass. It was observed that enzyme formulation produced high sugar yields. With switch grass as the biomass, 520 g sugar/kg biomass was released after enzymatic hydrolysis, while 410 g sugar/kg biomass is normally released (Bals et al., 2010).

3.1.3. Chemical pretreatment

3.1.3.1. Acid pretreatment

This process is used more often than biological or physical pretreatment methods because it is more effective and enhances the biodegradation of complex materials (Zhou, Zhang, & Dong, 2012). In this method, dilute sulfuric acid (H_2SO_4) is the most commonly used (Us & Perendeci, 2012), because it has high efficiency in the separating process of cell wall components resulting in hemicellulose hydrolysate and cellulignin (Bardone et al., 2014; Harmsen et al., 2010; Pandey, Larroche, Ricke, Dussap, & Gnansounou, 2011). However, other acidic substances such as hydrochloric acid (HCl) (Pakarinen, Kaparaju, & Rintala, 2011), oxalic acid ($C_2H_2O_4$) (Anuj K Chandel, Silva, Singh, Silvério, & Singh, 2012), and acetic acid (CH_3COOH) (Monlau, Latrille, Da Costa, Steyer, & Carrère, 2013) have also shown promising results. The process can be performed at temperature ranges of between 120 ℃ and 180 ℃ and residence times ranging between 15 min and 60 min. The low temperature for this process makes it a low cost pretreatment, and it can at least loosen the cell wall matrix through hemicellulose degradation (Alvira, Tomás-Pejó, Ballesteros, & Negro, 2010). The process does not affect lignin, but cellulose microfibrils are sufficient to produce a high yield of monomeric sugars for fermentation (Taherzadeh & Karimi, 2008; Vohra, Manwar, Manmode, Padgilwar, & Patil, 2014). In a similar study, Tang et al. (2013) employed acid pretreatment of *Eulaliopsis binate* using dilute sulfuric acid. It was found that 21.02 % of total sugars were produced with low inhibitor levels after being pretreated by 0.5 % dilute sulfuric acid at 160 ℃ for 30 min and at a solid-to-liquor ratio of 1:5.

Inhibitor formation and the hydrolysis of lignocellulose are a function of pretreatment severity, which is influenced by the acid concentration, reaction temperature, and retention time. Overend et al. (Overend, Chornet, & Gascoigne, 1987) developed an equation that involves the reaction time and temperature, which indicates the severity of the pretreatment by combined severity factor (CSF). These relationships are indicated in equation (1).

$$CSF = t_{exp}\left[\frac{(T - T_{ref})}{14.75}\right] \tag{1}$$

Where t is the residence time (min); T is the temperature (℃), and T_{ref} is the reference temperature, usually set to 100 ℃.

3.1.3.2. Alkali pretreatment

This pretreatment process is applied in a simple operation and gives high conversion yields within only a short period (Harmsen et al., 2010). This process utilizes lower temperatures and pressures than other pretreatment technologies (Yi Zheng et al., 2009) and causes less sugar degradation, but the inhibitors are usually eliminated in order to optimize the pretreatment conditions (Canilha et al., 2012). Alkali reagents such as potassium hydroxide (KOH), sodium hydroxide (NaOH), hydrazine (N_2H_2), anhydrous ammonia (NH_3) and calcium hydroxide $Ca(OH)_2$ are typically featured in alkali pretreatment of biomass (Sebayang et al., 2016). The pretreatment process using sodium hydroxide (NaOH) is one of the most effective chemical pretreatments for ethanol production (J. S. Kim, Lee, & Kim, 2016) and can enhance the swelling characteristics, which is accompanied by a higher accessible area (Keikhosor Karimi, Shafiei, & Kumar, 2013), as well as cause a decrease in crystallinity and polymerization degree (Mosier et al., 2005). In general, this pretreatment is more effective on the hardwood, herbaceous crops, and agricultural residues with low lignin content and high lignin content in softwood (Bjerre, Olesen, Fernqvist, Plöger, & Schmidt, 1996). Playne (Playne, 1984) pretreated rice straw using alkali chemicals (NaOH, $Ca(OH)_2$ and KOH) in 24 h at 25 ℃, and found that NaOH (6% chemical loading, g/g dry rice straw) was the best alkali chemical to

achieve 85% increase of glucose yield by enzymatic hydrolysis. Bali et al. (Bali, Meng, Deneff, Sun, & Ragauskas, 2015) studied the effect of different pretreatment methods and found that the highest increase in cellulose accessibility was with dilute NaOH solution, followed by methods using NH_4OH soaked in $Ca(OH)_2$ solution.

3.1.3.3. Ozonolysis pretreatment

Ozone (O_3) is a powerful oxidant, soluble in water and is readily available. It is highly reactive toward compounds incorporating conjugated double bonds and functional groups with high electron densities. The most likely biomass constituent to be oxidized is lignin due to its high content of C=C bonds (García-Cubero, González-Benito, Indacoechea, Coca, & Bolado, 2009). Ozone is used to degrade the lignin and hemicellulose fractions from many lignocellulosic materials such as bagasse, wheat straw, pine, peanut, cotton straw, and poplar sawdust (P. Kumar et al., 2009). Ozonolysis cleaves carbon-carbon bonds which can occur at high temperatures or in catalytic beds; hence less pollution is ejected into the environment (P. Kumar et al., 2009). Gitifar et al. (2013) employed the ozonization of sugarcane bagasse previously treated with diluted sulfuric acid in an autoclave. The results showed that delignification and sugar production increased by applying the acid pretreatment; no data about degradation compounds was provided. Travaini et al. (Travaini, Otero, Coca, Da-Silva, & Bolado, 2013) studied the effect of sugarcane bagasse in a fixed bed reactor. It was found that a 46 % of glucose yield was obtained at 80 % (w/w) moisture content, six percentage points more than at 40 % (w/w) moisture content, and concluded that low water content favored inhibitory compound formation. Karunanithy et al. (2014) reported that sequential extrusion-ozone pretreatment improved sugar recoveries. When compared with control samples, glucose, xylose, and total sugar recovery rates attained increases of 3.42, 5.01, and 3.42 times for switchgrass and of 4.5, 2.7, and 3.9 times for big bluestem.

3.1.3.4. Ionic Liquids (ILs)

Ionic liquids (ILs) are organic salts composed of organic cations and either organic or inorganic anions. Four groups of cations are mainly used for categorizing ionic liquids: quaternary ammonium, N-alkylpyridinium, N-alkyl-isoquinolinium, and 1-alkyl-3-methylimidazolium (C. Z. Liu, Wang, Stiles, & Guo, 2012). Besides being a powerful solvent for cellulose, ILs have unique properties such as low vapor pressure and high thermal and chemical stability. The desired property is adjustable by the selection of appropriate cations and anions (Keikhosor Karimi et al., 2013). Other factors to be considered when choosing an IL for pretreatment are the price, physical properties, availability, toxicity, corrosivity, biodegradability, and water tolerance (P. Mäki-Arvela, Anugwom, Virtanen, Sjöholm, & Mikkola, 2010). Among the ILs, [EMIM][Ac] and [BMIM][Cl] are mostly used for pretreatment of lignocellulosic materials, and efficient solvents for lignocelluloses (P. Mäki-Arvela et al., 2010). Certain ILs can cause cellulose dissolution, structural modification, and even its direct hydrolysis (C. Z. Liu et al., 2012). Residual ILs remaining in the biomass could interfere with hydrolytic enzyme activities and downstream fermentation steps (Sathitsuksanoh, Zhu, & Zhang, 2012; Shi et al., 2013). It may affect the final sugar and biofuel yields. After regeneration, ILs can be recovered from anti-solvents by flash distillation and be reused (Joglekar, Rahman, & Kulkarni, 2007).

3.1.4. Biological pretreatments

Biological pretreatment of LCB is considered an efficient, eco-friendly and cheap alternative (Wan & Li, 2012). There are several microorganisms which can naturally assimilate inhibitory compounds, including yeasts (*Saccharomyces cerevisiae*), fungi, and bacteria (Parawira & Tekere, 2011). Some microorganisms during incubation are able to release cellulase and hemicellulase and degrade only lignin, resulting in a lignocellulosic substrate which can be

easily hydrolyzed into fermentable sugars with mild conditions and in a short time (A K Chandel, Chandrasekhar, Radhika, & Ravinder, 2011). The commonly used microorganisms are filamentous fungi which are ubiquitous and can be isolated from the soil, living plants or lignocellulosic waste material (Vats, Maurya, Shaimoon, Agarwal, & Negi, 2013). Generally, wood degrading microorganisms like bacteria and brown rot, white rot, and soft rot fungi are employed in biological pretreatment (Hage et al., 2009). Fungi have distinct degradation characteristics on LCB. Brown rot fungi mainly attack cellulose, while white and soft rot fungi attack both cellulose and lignin (Sun & Cheng, 2002). The advantages and disadvantages of different pretreatment processes for LCB materials are summarized in Table 1.

Table 1 Advantages and disadvantages of different pretreatment processes for lignocellulosic biomass materials.

PRETREATMENT METHOD	PROCESS	ADVANTAGES	DISADVANTAGES	REFERENCE
Physical	Mechanical: Physical reduction in substrate particle size by grinding, milling, etc.	Reduces cellulose crystallinity and degree of polymerization Reduced the particle size to increase a specific surface area	Power consumption usually higher than inherent biomass energy	(Balat, 2011)
Physico-chemical	Steam explosion: Substrate particles rapidly heated by high-pressure saturated steam. Explosive decompression caused by quick release of pressure acids released to aid in hemicellulose hydrolysis.	Cost-effective Causes lignin transformation and hemicellulose solubilization High yield of glucose and hemicellulose in the two-step process	Partial hemicellulose degradation Toxic compounds generation Acidic catalyst needed to make the process efficient with high lignin content material	(Brodeur et al., 2011)
	Ammonia fiber explosion (AFEX): Substrate is exposed to hot liquid ammonia under high pressure. Pressure is released suddenly breaking open biomass structure.	Increases accessible surface area Fewer inhibitors formation Does not require a small particle size of biomass	Very high pressure requirements Expensive Not very effective for the biomass with high lignin content	(Gumisiriza, Hawumba, Okure, & Hensel, 2017)
	CO2 explosion: Injected to the biomass reactor in very high pressure and heated at high temperature.	Increases accessible surface area Non-flammability Do not form inhibitory compounds Availability at relatively low cost	Very high pressure requirements A portion of xylan fraction lost It can emit the CO2 emission to the atmosphere	(Maurya et al., 2015; Sebayang et al., 2016)

PRETREATMENT METHOD	PROCESS	ADVANTAGES	DISADVANTAGES	REFERENCE
		Easy recovery after extraction and environmental acceptance		
Chemical	Acid: Addition of dilute or concentrated acid solutions result in hemicellulose hydrolysis (H2SO4, HCl, HNO3, H3PO4).	High glucose yield High concentration can be done at room temperature Solubilizes hemicellulose	High operational and maintenance costs Corrosive Formation of inhibitors Concentrated acids are toxic and hazardous	(A. K. Kumar & Sharma, 2017)
	Alkali: Addition of base causes swelling, increasing the internal surface of cellulose which provokes lignin structure disruption (NaOH, KOH, Lime, Mg(OH)2, NH4OH).	Decreased cellulose crystallinity and degree of polymerization Can be done at room temperature Efficient removal of lignin	Relatively expensive Not used for large scale plant Irrecoverable salts formed and incorporated into biomass	(Bali et al., 2015; Rabemanolontsoa & Saka, 2016)
	Ozonolysis: Powerful oxidant, soluble in water and is readily available.	Reduces lignin content Does not produce toxic residues No requirement of chemical additives Operation at ambient temperature and pressure	Relatively expensive due to a large amount of ozone generated Highly reactive, flammable, corrosive and toxic characteristics of ozone	(Travaini, Martín-juárez, Lorenzo-hernando, & Bolado-rodríguez, 2016)
	Ionic Liquids (ILs): Organic salts composed of organic cations and either organic or inorganic anions ([EMIM][Ac], [BMIM][Cl]).	Highly efficient (over 80 % saccharification yield) Environmental friendly chemicals Minor degradation of raw materials Negligible production of inhibitory compounds	Very expensive Has negative effects on cellulose activity and affect the final yield of cellulose hydrolysis Consume much water	(Keikhosor Karimi et al., 2013)
Biological	Fungi and actinomycetes: Microorganisms degrade and alter biomass structure (white-, brown-, soft-rot fungi).	Low energy consumption Simple equipment degrades lignin and hemicelluloses	A rate of hydrolysis is very low Low degradation rate to attain a high degree of lignin degradation	(P. Kumar et al., 2009)

PRETREATMENT METHOD	PROCESS	ADVANTAGES	DISADVANTAGES	REFERENCE
		Relatively inexpensive Does not cause corrosion to the equipment Low production of inhibitors		

3.2. Hydrolysis

Pretreatment is a crucial step for any lignocelluloses before hydrolysis (saccharification). Different pretreatments have been reported in the literature which makes substrates more conducive for hydrolysis. Researchers have recently reported many different methods for the hydrolysis of LCB materials. The most commonly applied methods are classified into two groups: enzymatic hydrolysis and acid hydrolysis (dilute and concentrated).

3.2.1. Enzymatic hydrolysis

Enzymatic hydrolysis uses enzymes (cellulases and xylanases) to hydrolyze cellulose and hemicellulose to fermentable sugars (Jain, Dey, Kumar, & Kuhad, 2015). The major challenge for ethanol production is the cost of producing the enzyme complexes (Laisa dos Reis et al., 2013; Laísa dos Reis, Schneider, Fontana, Camassola, & Dillon, 2014; G. Liu, Zhang, & Bao, 2016). However, the advancement of technologies in enzyme manufacturing is likely to bring about a reduction in enzyme price. There are many reports of the commercial applications of lignocellulolytic enzymes, especially cellulase. The production of enzymes, for instance, cellulase, can be extracted from fungi and bacteria. The main fungi involved include: *Trichoderma reesei* (Brethauer & Studer, 2014; Martins, Kolling, Camassola, Dillon, & Ramos, 2008; Wu et al., 2016), *Penicillium echinulatum* (Camassola & Dillon, 2014; Scholl et al., 2015), *Thermoascus aurantiacus* (Jain et al., 2015), *Trichoderma longibrachiatum* (Shaibani, Yaghmaei, Andalibi, & Ghazvini, 2012), and *Trichoderma viride* (Nathan, Rani, Rathinasamy, Dhiraviam, & Jayavel, 2014). Meanwhile, the typical cellulase-producing bacteria include *Acetivibrio* (Du et al., 2015), *Bacteriodes* (Elshaghabee et al., 2016), *Bacillus* (Romero, Merino, Bolívar, Gosset, & Martinez, 2007)*, Cellulomonas* (Kojima, Okamoto, & Yanase, 2013)*, Clostridium* (Patankar, Dudhane, Paradh, & Patil, 2018)*, Erwini* (Tolan & Finn, 1987)*, Ruminococcus* (Yanning Zheng, Kahnt, Kwon, Mackie, & Thauer, 2014)*, Streptomyces* and *Thermomonospora* (Ventorino et al., 2016).

Various factors affect enzymatic hydrolysis, namely: substrates, cellulase activity, reaction conditions (temperature, pH as well as other parameters), and a strong product inhibition (Balat, 2011). To improve the yield and rate of enzymatic hydrolysis, research has been focused on optimizing the hydrolysis process and enhancing cellulase activity (Sun & Cheng, 2002). The rate of enzymatic hydrolysis is dependent upon several structural parameters of the substrate (Pan, Gilkes, & Saddler, 2006). The parameters known to affect the rate of hydrolysis include: (1) molecular structure, (2) crystallinity, (3) surface area of the fiber, (4) degree of swelling of the fiber, (5) degree of polymerization, and (6) associated lignin or other materials (Detroy & St Julian, 1982).

Selig et al. (Selig et al., 2012) reported that commercial enzymatic cocktails often come with relatively high amounts of preservatives such as glycerol and sorbitol which have a negative effect on enzymatic hydrolysis. Arumugam and Manikandan (Arumugam & Manikandan, 2011) studied the potential application of pulp and banana peel wastes in

bioethanol production using dilute acid pretreatment followed by enzymatic hydrolysis. Cha et al. (Cha et al., 2014) pretreated *Miscanthus sinensis* grass using enzymatic hydrolysis with 20 FPU/g cellulose at 50 °C for 72 h and obtained 93.6 % with 31.2 g/L glucose by combined pretreatment of ammonia and CO_2. Agudelo et al. (Agudelo, García-Aparicio, & Görgens, 2016) found that the highest cellulose saccharification (92 %) of triticale straw was as a result of steam explosion pretreatment at 200 °C for 10 min. Recent research by Patankar et al. (Patankar et al., 2018) obtained the maximum reducing sugars of 205 mg/g from corncobs and 100 mg/g from soybean cake as a result of treatment with 100 IU cellulase for 48 h with 28 % saccharification efficiency. The most recent comparative results of enzyme hydrolysis with individual sugars and total reducing sugars are shown in Table 2. The hydrolysis yield (%) can be calculated using Equation 2 (Salehian & Karimi, 2013).

$$Hydrolysis\ yield\ (\%) = \frac{Produced\ glucose\ (g/L)}{1.111 \times glucan\ in\ sample\ (g/L)} \times 100 \qquad (2)$$

Where the conversion factor of 1.111 was applied for hydration of glucan to glucose.

3.2.2. Acidic hydrolysis

Acidic hydrolysis can be divided into two types namely dilute and concentrated. Dilute acid hydrolysis is performed at a higher temperature using a low acid concentration while concentrated acid hydrolysis is carried out at a lower temperature using a high acid concentration. Dilute acid hydrolysis is the most commonly used process (Mohd Azhar et al., 2017) because it generates a large number of inhibitors compared to concentrated acid hydrolysis (Mohd Azhar et al., 2017). The goal of dilute acid hydrolysis is to remove hemicellulose selectively. The hydrolysis products may contain large oligomers. In this process, biomass can be hydrolyzed in a temperature range of 120 °C to 220 °C using dilute sulfuric acid (H_2SO_4) as a catalyst. Under these conditions, nearly selective hydrolysis of hemicelluloses can be achieved, since it forms less glucose (Marzialetti et al., 2008). However, the optimum reaction conditions are selected from several interrelated parameters such as time, acid concentration, type of biomass and its concentration, making the comparison of different parameters difficult (Päivi Mäki-Arvela, Salmi, Holmbom, Willför, & Murzin, 2011b).

Many studies have been carried out to investigate the effect of dilute as well as concentrated acid and enzymatic hydrolysis from different biomass sources (as reported in Table 3). Velásquez-Arredondo et al. (2010) investigated the acid hydrolysis of banana pulp and fruit and the enzymatic hydrolysis of flower stalk and banana skin, and the results obtained demonstrated a positive energy balance for the four production routes evaluated. Karimi et al. (2006) employed high pressure two-stage dilute acid hydrolysis (1.0 % H_2SO_4 in the first stage and 0.5 % H_2SO_4 in the second) to obtain high conversion of 189 g xylose per kg and 29 g glucose per kg and considerable amounts of furfural and HMF of the rice straw used. Chamy et al. (1994) identified the best conditions for sugar beet pulp hydrolysis to be 1.1 g H_2SO_4/g sugar beet pulp at 80 °C for 90 min. Under such conditions, 86.3 % and 7.8 % of cellulose and hemicellulose hydrolysis, respectively, were obtained. In addition, untreated elephant grass is similar in cellulose composition to sugarcane bagasse, at around 36 % cellulose (Menegol, Scholl, Fontana, Dillon, & Camassola, 2014), while sugarcane bagasse contains 34 % to 45 % cellulose (Szczerbowski, Pitarelo, Zandoná Filho, & Ramos, 2014).

3.3. Fermentation

This is a process of converting biomass into bioethanol by microorganisms such as yeast, fungi, and bacteria, which digest fermentable sugars and produce ethyl alcohol and other byproducts (Vohra et al., 2014). After pretreatment, the next steps are hydrolysis and fermentation, which can be carried out separately or simultaneously. The following processes are commonly used

in the production of bioethanol: separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), and simultaneous saccharification and co-fermentation (SSCF) (Mohd Azhar et al., 2017). *Saccharomyces* and *Pichia* are the most common hexose and pentose-fermenting yeasts used in bioethanol production under different conditions of fermentation (Tesfaw & Assefa, 2014), as well as the bacteria *Zymomonas* and *Escherichia* and *Aspergillus* (Skotnicki, Warr, Goodman, Lee, & Rogers, 1983). Most studies have employed *S. cerevisiae* as their microorganism. Yu and Zhang (2003) compared the ethanol yield by *S. cerevisiae*, *Pichia* sp. YZ–1 and *Z. mobilis* and obtained a maximal ethanol yield of 0.45 g/g glucose by *S. cerevisiae*. Khawla et al. (2014) produced bioethanol from potato peel using both acid and enzyme hydrolysis. It was concluded that potato peel hydrolysate obtained from enzyme hydrolysis produced a higher ethanol yield compared to acid hydrolysate fermented by *S. cerevisiae*. This shows that the construction of engineered *S. cerevisiae* expressing cellulose is an important approach to degrading LCB materials (Kroukamp, den Haan, van Zyl, & van Zyl, 2018).

The most recent studies on ethanol production from different LCB materials using enzymatic hydrolysis and fermentation by *S. cerevisiae* are reported in Table 3. Ethanol yield can be calculated as a percentage of theoretical yield using Equation 3 (Bahmani, Shafiei, & Karimi, 2016).

$$Ethanol\ yield\ (\%) = \frac{Ethanol\ produced\ (g/L)}{1.111 \times initial\ weight\ of\ biomass\ in\ the\ fermentation\ medium\ (g/L) \times 0.51 \times glucan\ in\ sample\ (g/L)} \times 100$$

(3)

This review paper compares the types of fermentation processes, and each of the processes is discussed below.

3.3.1. Simultaneous saccharification and fermentation (SSF)

The process in which the cellulose is broken down and fermented at the same time in the presence of the microorganism is called simultaneous saccharification and fermentation (SSF) (South, Hogsett, & Lynd, 1993; Sun & Cheng, 2002). In SSF, the fungal cellulases are most active at 50 °C to 55 °C, while the microbes ferment effectively at temperatures below 35 °C (Brodeur et al., 2011). This fermentation process has been the preferred step for the production of biofuels and chemicals because the operations of both hydrolysis and fermentation are conducted in the same reactor vessel thus reducing costs (Brodeur et al., 2011). This utilizes the sugars by fermenting organisms that could reduce the extent of feedback inhibition of enzymes and chances of contamination are also minimal due to the presence of ethanol in SSF (Stenberg, Bollók, Réczey, Galbe, & Zacchi, 2000). However, the major disadvantage is that both saccharification and fermentation are carried out under suboptimal conditions (Galbe & Zacchi, 2002). Fig. 5 describes the process of SSF.

Park et al. (2010) produced an ethanol yield of 74 % of the theoretical value using a mixture of *S. cerevisae* and *Pichiastipitis* after 79 h of fermentation at 30 °C using the SSF process. Oberoi et al. (2011) optimized the bioethanol production from banana peels using enzyme hydrolysis and SSF by *S. cerevisiae*. Boluda-Aguilar et al. (2010) produced bioethanol from mandarin peel waste and obtained 6.8 g ethanol per 100 g biomass using SSF and the *S. cerevisiae* CECT1329 strain. The advantages and disadvantages of the SSF process as found by researchers are reported in Table 2.

Figure 5 The schematic process of the simultaneous saccharification and fermentation (SSF) (Sebayang et al., 2016).

3.3.2. Simultaneous saccharification and co-fermentation (SSCF)

The SSCF fermentation technique utilizes the integration principle in employing mixed microbes to ferment more than one sugar type such as pentoses and hexoses (Buruiana, Garrote, & Vizireanu, 2013; Sarkar et al., 2012). For the conversion of both pentoses and hexoses to ethanol, separate hydrolysis and co-fermentation (SHCF) or simultaneous saccharification and co-fermentation (SSCF) has been suggested (Dien, Cotta, & Jeffries, 2003). The use of mixed microbes is limited by the respective ability of the microbes hexose-fermenting microbes usually grow faster than pentose-fermenting microbes, and this leads to a higher rate of ethanol conversion from hexose (Sebayang et al., 2016).

Xylose assimilation in the former process suffers from glucose and ethanol inhibition (Jin, Gunawan, Balan, Lau, & Dale, 2012). SSCF can be performed by two different or one recombinant microorganism (R. Kumar, Tabatabaei, Karimi, & Sárvári Horváth, 2016). In SSCF, glucose inhibition is reduced; however, ethanol yield in SSCF from both glucose and xylose is considerably lower than that formed from glucose by ordinary yeasts (e.g., *S cerevisiae*) (Koppram et al., 2013). This fermentation technique holds several beneficial characteristics (as reported in Table 2). According to the reviewed literature, cellulose hydrolysis can also coincide with fermentation in the presence (SScF) or absence (SSF) of hemicellulose. Fig. 6 shows the schematic process of simultaneous saccharification and co-fermentation (SSCF).
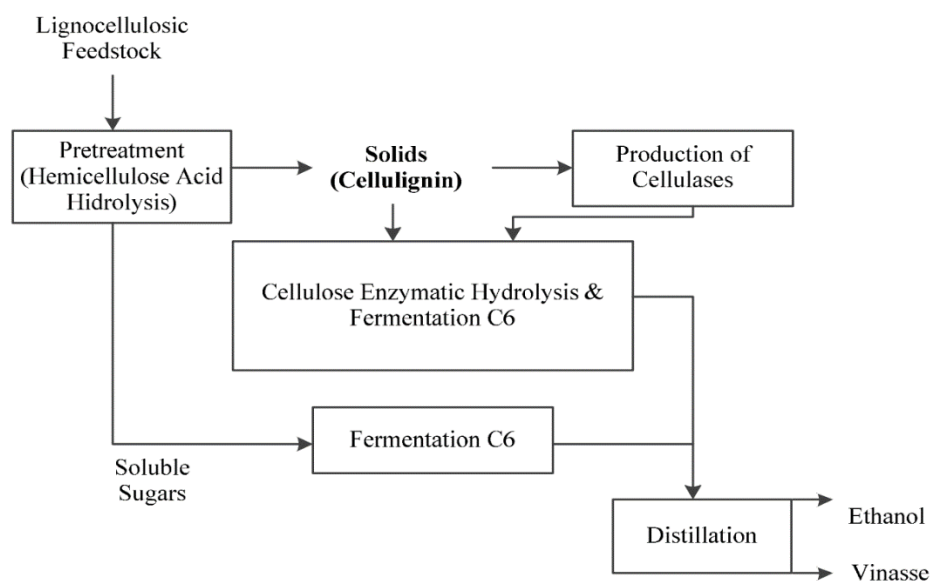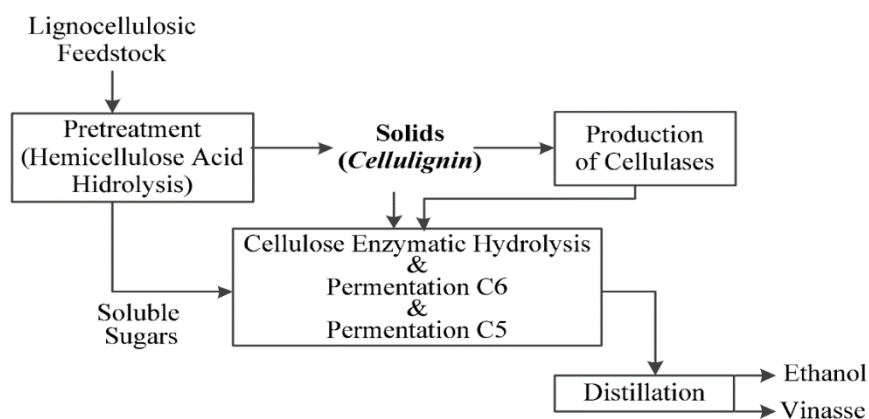
Figure 6 The schematic process of the simultaneous saccharification and co-fermentation (SSCF) (Sebayang et al., 2016).

3.3.3. Separate hydrolysis and fermentation (SHF)

In SHF, hydrolysis of LCB is performed separately from the fermentation step. In this process, each step can be conducted at optimal conditions of pH and temperature. However, glucose and cellobiose accumulation in the hydrolysis step inhibits the activity of the cellulases (Stenberg et al., 2000; Xiao, Zhang, Gregg, & Saddler, 2004). SHF and SSF are complementary to one another in Table 2. This combination can be used for economic assessment and process optimization of the production process of ethanol from lignocellulosic materials. Fig. 7 presents a model which illustrates the process of separate hydrolysis and fermentation.

Choi et al. (2013) used the SHF process and obtained a maximum of 29.4 g ethanol from 100 g mandarin peel waste using popping pretreatment and enzyme hydrolysis supported by the *S. cerevisiae* KCTC 7906 strain. In summary (as reported in Table 3), the most recent bioethanol production studies focus on utilizing agriculture residues, where both SSF and SHF techniques are used to produce ethanol. Almost 84 % of the studies cited used *S. cerevisiae* as a biocatalyst for fermentation. Table 3 shows that unripe banana peel (Prakash, Chauhan, General, & Sharma, 2018; Waghmare & Arya, 2016), *Matooke* peels (Yusuf & Inambao, 2019a), *Agave tequilana* bagasse (Aguilar et al., 2018; Rios-González et al., 2017), banana peels (*Tabasco* variety) (Palacios et al., 2017), *A. salmiana* (Flores-Gómez et al., 2018), *G. verrucosa* (Sukwong et al., 2018), empty palm fruit bunch fiber (S. Kim, 2018), rice straw (Bahmani et al., 2016), switchgrass (Papa et al., 2015), and corn stover (Uppugundla et al., 2014) all have a high ethanol yield, and are suitable for commercial bioethanol production in different locations or regions. This classification of bioethanol fuel from different lignocellulosic materials and processes are currently being developed to meet sustainability and fuel quality standards, as well as the need for roads, aviation, and electricity.
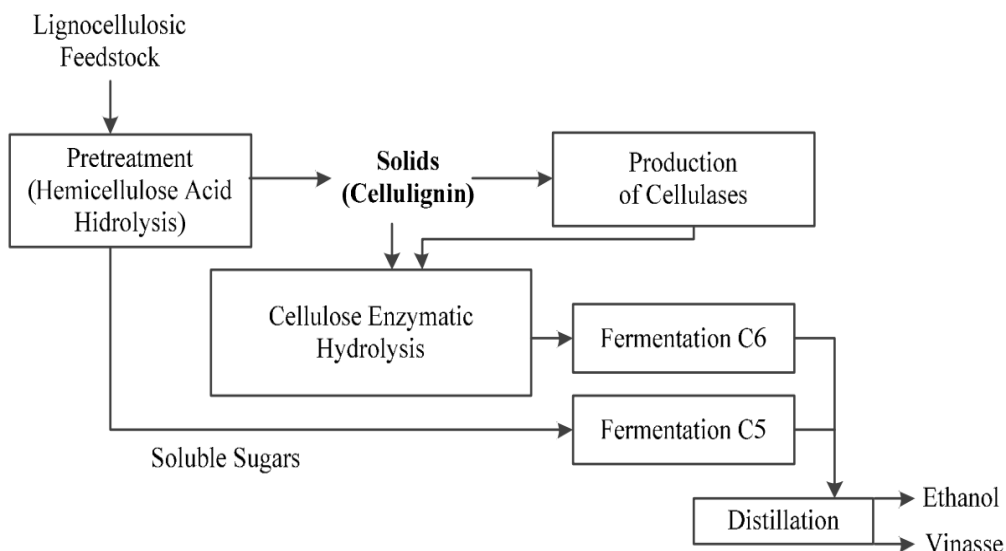
Figure 7 The schematic process of the separate hydrolysis and fermentation process (SHF) (Sebayang et al., 2016).

Table 2 Advantages and disadvantages of separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF) and simultaneous saccharification and co-fermentation (SSCF).

Fermentation processes	Advantages	Disadvantages
Separate hydrolysis and fermentation (SHF)	Ability to carry out each step under optimal conditions, i.e., enzymatic hydrolysis at 45 °C to 50 °C for better performance and fermentation at 30 °C for optimizing sugar utilization (Mohd Azhar et al., 2017; Tengborg, Galbe, & Zacchi, 2001). SHF is more efficient than SSF when bioethanol production is carried out using cellulosic biomass (Cotana et al., 2015; Wirawan, Cheng, Kao, Lee, & Chang, 2012). The yeast produced during the SHF process can be recycled after fermentation of the hydrolysate, which is not possible in SSF (Olofsson, Bertilsson, & Lidén, 2008).	Inhibition of cellulase and β-glucosidase enzymes by glucose released during hydrolysis, which calls for lower solids loadings and higher enzyme loadings to achieve reasonable yields (Balat, 2011).
Simultaneous saccharification and fermentation (SSF)	Lower enzyme requirements; higher product yields; lower requirements for sterile conditions since glucose is removed immediately and bioethanol is produced; shorter process time; and less reactor volume (Sun & Cheng, 2002). The immediate consumption of sugars by the microorganism produces low sugar concentrations in the fermentor, which significantly reduces enzyme	The conditions of SSF are more difficult to optimize (Krishna, Reddy, & Chowdary, 2001). During SSF the release of sugar is not controlled, as all the cellulase enzymes are added at once (Erdei, Frankó, Galbe, & Zacchi, 2012).

Fermentation processes	Advantages	Disadvantages
	inhibition compared to SHF (Schell Mark F.; Tucker, Melvin P., 1999). This process is often effective when combined with dilute acid or high temperature hot-water pretreatment (Balat, 2011). Accept the mode of improvement which combines the cellulase enzymes and fermenting microbes in one vessel to improve the bioethanol production economics (Y. Yu, Lou, & Wu, 2008).	
Simultaneous saccharification and co-fermentation (SSCF)	Reduced capital costs (Wingren, Galbe, & Zacchi, 2003). Continuous removal of end-products of enzymatic hydrolysis that inhibit cellulases or β-glucosidases (Olofsson et al., 2008). Higher ethanol productivity and yield than separate hydrolysis and fermentation (Alfani, Gallifuoco, Saporosi, Spera, & Cantarella, 2000; Tomás-Pejó, Oliva, Ballesteros, & Olsson, 2008). Maintains glucose at low levels allowing efficient co-fermentation of glucose and xylose (Öhgren et al., 2006).	At high water insoluble solids (WIS) content, the ethanol yield decreases due to an increase in mass transfer resistance and inhibitors concentration (Hoyer, Galbe, & Zacchi, 2009).

Table 3 Different methods, conditions and their effects for bioethanol from various biomasses (reported between the years 2013 to 2019).

Biomass	Pretreatment conditions	Hydrolysis conditions	Sugar yield	Fermentation conditions	Results: Ethanol yield	Remarks	Reference
Energy grass	Alkali: 100 ml of 1 % (w/v) NaOH at 121 °C for 1h	Enzymatic hydrolysis by Cellic® CTech with 0.1 g/g grass at 50 °C, 150 rpm, pH 4.8 for 72 h	467.9 mg/g	-	-	Ozonolysis is an efficient pretreatment method for energy grasses, resulting in up to 51 % delignification.	(Panneerselvam, Sharma-Shivappa, Kolar, Clare, & Ranney, 2013)
	Ozonolysis: performed for 2h at a flow rate of 0.25 l/min		431.9 mg/g	-	-		
Corn stover	DA: H_2SO_4 of 5 CL with 895.5 kg of H_2O at 160 °C for 20 min and N-CR	Biomass: 29 kg glucan, CTec2: 583 g, HTec2: 287 g at	65 g/L of glucose[a] and 4 g/L of xylose in 72 h	*S. cerevisiae* strain 424A (LNH-ST), 0.28 g dry-cell-wt./L and operated	14 kg	AFEX produces high digestible substrates, high fermentation	(Uppugundla et al., 2014)

Biomass	Pretreatment conditions	Hydrolysis conditions	Sugar yield	Fermentation conditions	Results: Ethanol yield	Remarks	Reference
		50 °C with pH 4.8 for 72 h		for 120 h (SSF)		metabolic yield with 98 %.	
	IL: [C2mim][OAc] of 900 CL at 140 °C for 180 min and CR	Biomass: 31.7 kg glucan, CTec 2: 371 g, HTec 2: 314 g, Multifect Pectinase: 266 g at 50 °C with pH 4.8 for 72 h	72 g/L of glucose[b] and 35 g/L of xylose in 72 h		21.2 kg		
	AFEX: Anhydrous ammonia of 100 CL with 60 kg of H_2O at 140 °C, 300 psi for 15 min and CR	Biomass: 33.5 kg glucan, CTec 2: 670 g, HTec 2: 167.5 g, Multifect Pectinase: 167.5 g at 50 °C with pH 4.8 for 72 h	60 g/L of glucose[c] and 29 g/L of xylose in 72 h		20.5 kg		
Sugarcane bagasse	Acid: H_2SO_4 of 1 % (w/v), 1:10 solid-liquid ratio at 121 °C for 20 min.	Hydrolyzed by dilute acid (2.0 % of H_2SO_4) at 155 °C for 10 min	Glucose 22.74 g/L, no xylose	*S. cerevisiae* stain NRRL Y-7124 at 30 °C, 200 rpm for 72 h	16.8 g/L conc., 0.38 g/g and 0.23 g/L/h productivity	This process generates inhibitory compounds, and the detoxification was required for removing those compounds found in the hydrolysate.	(Bardone et al., 2014)
Switchgrass	IL: Pretreated with [C2C1Im][OAc] at 100 °C for 3 h	Hydrolysis by cellulase of *novozyme* HTec2 at 0.3 % w/w (g	20 g/L glucose	*S. cerevisiae* strain BY4741 at 30 °C, 200 rpm for 20 h	85.7 g	IL pretreatment demonstrated higher bioethanol yields.	(Papa et al., 2015)

Biomass	Pretreatment conditions	Hydrolysis conditions	Sugar yield	Fermentation conditions	Results: Ethanol yield	Remarks	Reference
		enzyme/g xylan), 30 min, 2 h, 6 h, 24 h and 48 h					
Wheat straw	Ozonolysis: Pretreated for 1 and 7 h at 0.6 l/min flow rate with ambient conditions	Enzymatic hydrolysis was performed for 72 h	Glucose of 49 % and xylose of 9.14 %	(SSF) was performed for 140 h	12.9 g/L and 67 % conc.	Results showed that ozone (or PAP) not only degraded lignin but also had an effect on epicuticular waxes on wheat straw.	(Kádár et al., 2015)
Rice straw	BP: Pretreated substrates in 30 mL of 50 mM sodium citrate buffer (pH = 4.8)	Hydrolysis was conducted using 90 % v/v Cellic® CTec2 and 10 % v/v Cellic® HTec2 and 30 FPU/g cellulase and 50 IU/g β-glucosidase at 45 °C and 120 rpm for 72 h.	69.5 % of hydrolysis yield	S. cerevisiae (CCUG 53310) at 37 °C and 130 rpm for 24 h through (SHF)	206 g	Increasing the porosity of the substrate by hemicellulose removal could be the main effective parameter in this type of pretreatment. However, enzymatic hydrolysis and ethanol production processes need to be improved.	(Bahmani et al., 2016)
Banana peels	MP and SE: pretreated with autoclaved at 15 psi pressure for 30 min, knife milling with 2 cm to 4 cm and dried at 60 °C	0.5 % (v/v) to 2.5 % (v/v) diluted sulfuric acid 70 °C and 110 °C, pH 7 for 10 min to 30 min	11 g/L glucose and 5.5 g/L xylose	S. cerevisiae strain at 30 °C, 200 rpm for 24 h	45.088 % of bioethanol	The waste (banana peels) from the FPI may bring serious environmental problems. This can be minimized by the production of ethanol.	(Gebregergs, Gebresemati, & Sahu, 2016)
Unripe banana peel	MP: Dried at 60 °C for 24 h, electric grinder and sieved through mesh number 36 (0.45 mm).	Hydrolyzed by H_2SO_4 1 % (v/v) at 120 °C, 100 kPa for 10 min	49.2 % (w/w) of sugar release	S. cerevisiae (NCIM 3095, NCIM 3570 and NCIM 3059) at 30 °C, pH 5, 150 rpm for 36 h	35.5 g/L, 1.5 g/L/h productivity	S. cerevisiae NCIM 3095 was found to be the best strain for production of ethanol compared to the other two strains.	(Waghmare & Arya, 2016)
Elephant grass	MP: Dried at 60 °C for 3 days, 4 % to 20 % (w/v) in a concomitant ball milling treatment / triturated with forage chopper (0.5 cm to 2 cm).	124.43 U/mL, 6.16 U/mL and 893.55 U/ml of b-glucosidases, endoglucanases and xylanases at	12.47 g/L	S. cerevisiae CAT-1 at 28 °C for 48 h	6.1 g/L	High ethanol yield is not only to do with biomass but depends on enzymatic and fermentation processes. There	(Menegol, Fontana, José, Dillon, & Camassola, 2016)

Biomass	Pretreatment conditions	Hydrolysis conditions	Sugar yield	Fermentation conditions	Results: Ethanol yield	Remarks	Reference
		50 °C, pH 4.8, 150 rpm for 1 h to 6 h				is a need to develop equipment for such purposes.	
Pine wood	Alkali: Performed with 0-2% w/v NaOH at 100-180 °C for 1 h to 5 h.	Enzymes mixture (90 % Cellic® CTec2 and 10 % Cellic® HTec2) at 1.5 FPU/g substrate of cellulase at 45 °C, pH 4.8, 120 rpm for 72 h	83.5 % ± 0.3 % glucose yield	*S. cerevisiae* under anaerobic conditions for 24 h	76.9 % to 78.0 % and 0.609 g/L/h ± 0.015 g/L/h productivity	Production of bioethanol requires cheap raw materials which can effectively enhance the manufacturing costs. Using chemicals for neutralization is unavoidable.	(Safari, Karimi, & Shafiei, 2017)
Cotton stalks	Alkali: NaOH (0.5 % to 4.0 % w/w) and the biomass loading (10 % to 25 %) at 120 °C for 20 min Acid: H$_2$SO$_4$ (0.5 % to 4.0 % w/w) and the biomass loading (10 % to 25 %) at 120 °C for 20 min	Hydrolysis by cellulose of *P. janthinellum* and 20 FPU/g substrate of cellulose at 50 °C, 200 rpm for 48 h	25.59 g/L of glucose and hydrolytic efficiency of 80 %	4 % (wet wt/v) *S. cerevisiae* RRP-03N at 30 °C ± 2 °C for 48 h, (SHF)	9 g	Alkali pretreatment of cotton stalks effectively de-lignified the biomass and a hydrolytic efficiency of 80 % was attained with a combination of commercial and in-house cellulases.	(Christopher, Mathew, Kiran Kumar, Pandey, & Sukumaran, 2017)
Agave tequilana bagasse	SE (AP): Pretreated at elevated temperatures (160 °C to 240 °C) no chemicals required but H$_2$O	Hydrolyzed using Cellic® CTec3 of 25 FPU/g of glucan at 50 °C, pH 4.8, 200 rpm for 72 h	131 g/L ± 1.7 g/L glucose and 81.5 % ± 1.7 % hydrolysis yield[d]	*S. cerevisiae* ATCC 4126 at 30 °C, pH 5.5, 100 rpm for 24 h (SHF)	65.26 g/L and 95 % of the theoretical value	AP can be an efficient and relatively simple method for *Agave tequilana* that can be incorporated in a 2nd GEPP.	(Rios-González et al., 2017)
Banana peels (*Tabasco* variety)	Acid and MP: H$_2$SO$_4$ (0 % v/v, 0.5 % v/v, 1% v/v), autoclaved at 121 °C, 103 kPa for 15 min, milled by mechanical grinding (1 mm).	15 FPU/g (Celluclast 1.5 L) 10 %, 15 % w/w), and 20 % (w/w) pretreated banana peel	32 g/L glucose	*Kluyveromyces marxianus* at 42 °C, 150 rpm for 24 h	21 g/L	The banana peel particle size control is not of great importance for the saccharification of this lignocellulosic material.	(Palacios et al., 2017)
A. tequilana			252 kg glucose and 109.8 kg xylose		154 kg ethanol	The amount of enzyme loading used in this experiment is higher; identifying the right combination of accessory enzymes in the future will further reduce the enzyme loading.	(Flores-Gómez et al., 2018)
A. salmiana	AFEX: 1000 kg solid, milling DM, Ammonia (2 kg NH**3**/kg DM) with 2kg of H2O at 102 °C to 120 °C for 30 min to 38 min	Cellic® CTec3 and HTec3 50 °C, pH 4.8, 250 rpm, and 72 h	301.4 kg glucose and 107 kg xylose	*Saccharomyces cerevisiae* 424A (LNH-ST) at 30 °C, 150 rpm, pH 5.5 for 72 h, (SHF)	176 kg ethanol		
Agave bagasse	SE/HP (AP): performed at 180 °C for 20 min, 40 min, and 50 min	*Novozymes* using 20 FPU/g of a substrate as	12.42 g/L glucose at 180 °C, 15.31 g/L Xylooligosacchari	*Saccharomyces cerevisiae* PE-2 at 30 °C, 150 rpm for 12 h	98.5 %[f], 99.5 %[e], 55.02 g/L of ethanol concentration	The result showed a decrease in the ethanol conc. on	(Aguilar et al., 2018)

Biomass	Pretreatment conditions	Hydrolysis conditions	Sugar yield	Fermentation conditions	Results: Ethanol yield	Remarks	Reference
		loading of cellulose at 150 rpm, pH 4.8, 180 °C for 20 min under IR and NIR	des and 65.87 % of IR	under (PSSF) and (SSSF)	and 90.84 % yield	a kinetic profile, due to ethanol evaporation during the production process, and the SSSF process was completed after 72 h.	
G. verrucosa	Acid: 12% (w/v) *G. verrucosa* with 0.2 M H_2SO_4 at 130 °C for 15 min	Celluclast 1.5 L, Viscozyme L, and Cellic CTec2 at 50 °C, 150 rpm for 48 h	50.7 g/L monosaccharides	*Pichia stipitis* and *Kluyveromyces marxianus* at 150 rpm at 30 °C	29.0 g/L ethanol, 0.81 g/L/h productivity	*P. stipitis* showed more efficient cell growth and bioethanol productivity than *K. marxianus.*	(Sukwong et al., 2018)
Banana peels	Acid: pretreated using HCl, pH 5.0.	Xylanase 1.99 IUm/L, FPase 2.0 IU m/L, pectinase 4.0 IU m/L, substrate (2.5 % to 20 %) at (60 °C to 90 °C), pH 9.0, 150 rpm for (1 h to 4 h).	37.06 mg m/L ORS at 70 °C	*Geobacillus stearothermophilus* strain HPA19 at 37 °C for 30 h	21.1 g/L, eff. of 76.5 % at 30 h	It is good to know the suitable ratio of cellulolytic and hemicellulolytic enzyme for different substrates to produce maximum reduction sugars.	(Prakash et al., 2018)
Orange peel	MP: milled with a grinding machine and dried	Cellulase 1.06 U/mL, 337.42 U/mL, and 1.36 U/mL at 37 °C for 18 h	20 g/L glucose	*S. cerevisiae* genome via the CRISPR-Cas9 approach at 30 °C, 180 rpm for 60 h (SSF)	7.53 g/L	The engineered strains may provide a valuable material for the development of lignocellulosic ethanol.	(Yang et al., 2018)
Sunflower stalk	IL: [Bmim]Cl 10 % to 25 % (w/w) pH 5.0, 60 °C for 24 h Alkali: NaOH 0.2 % to 2.0 %, (w/v), pH 5.0, 60 °C for 24 h IL and Alkali: NaOH 0.5 % w/v and [Bmim]Cl (25 %, w/w) 90 °C for 2 h	cellulase 20 FPU, and 400 IU of xylanase/g biomass at 50 °C for 72 h	302.4 mg/g glucose, 107 mg xylose, 114 mg/g reducing sugars	*P. oxalicum* PN8 (SSF)	(0.078 g/g biomass) of ethanol	Results showed that the combined IL and alkali pretreatment causes more drastic alterations in the biomass ultrastructure as compared to IL alone or alkali pretreatment.	(Nargotra, Sharma, Gupta, Kour, & Bajaj, 2018)
Empty palm fruit bunch fiber	Alkali-thermal: NaOH, dried sample (20 % w/v) at 105 °C for 24 h, autoclave (121 °C, 15 psi, 60 min)	(Celluclast 1.5 L), 20 FPU to 100 FPU and β-glucosidase (Novozyme 188; 40 CBU) for 72 h	82.2 % fermentable sugar conversion	*S. cerevisiae* W303-1A strain at 30 °C, 200 rpm for 28 h, (SHF)	33.8±0.5 g/L ethanol with 1.57 g/L/h productivity	Separate hydrolysis and fermentation using hydrolysate are useful for producing bioethanol with high productivity.	(S. Kim, 2018)
Matooke peels	MP: Dried at 58 °C for 83 h, 0.2 mm to 2 mm after milling and grinding with an electric grinder	0.5 % (v/v) to 2.5 % (v/v) of H_2SO_4, 50 °C to 90 °C ± 1 °C at 20 min to 60 min	77.03 g/L reducing sugars	*S. cerevisiae* NCIM 3570, at 29 °C to 39 °C ± 1 °C, 165 rpm, pH 5.0 for about 10 h to 30 h	71.54 g/L	Utilizing this waste biomass for bioethanol production through a biotechnological	(Yusuf & Inambao, 2019a)

Biomass	Pretreatment conditions	Hydrolysis conditions	Sugar yield	Fermentation conditions	Results: Ethanol yield	Remarks	Reference
		with gentle shaking				process not only helps to reduce environmental pollution but also reduces dependence on oil-producing countries.	

NOTE: [a] (88 % glucan conversion), [b] (100 % glucan conversion), [c] (79 % glucan conversion), [d] (at severity factor of 4.43), [e] (at high-solids loading), [f] (Saccharification yields), 2nd GEPP: Second generation ethanol production process, [Bmim]Cl: 1-butyl-3-methyl imidazolium chloride, [C2C1Im][OAc]: 1-ethyl-3-methylimidazolium, [C2mim][OAc]: 1-ethyl-3-methylimidazolium acetate, AbC: Aerobic condition, AFEX: Ammonia fiber expansion, BP: Biological pretreatment, CL: Catalyst loading of kg/100 kg dry biomass, CR: Catalyst recycled, DA: Dilute acid, DM: Dry materials, FPI: Food processing industry, FPU: Filter paper units, HP (AP): Hydrothermal processing (autohydrolysis process), IL: Ionic liquid, IR: isothermal regime, ORS: Optimum reducing sugar, MP: Mechanical pretreatement, NIR: non-isothermal regime, N-CR: No catalyst recycled, PAP: Plasma assisted pretreatment, SHF: Separate hydrolysis and fermentation, SSF: Simultaneous saccharification and fermentation.

4. BIOETHANOL AS ALTERNATIVE FUEL

The most common agricultural residues utilized for bioethanol production have been discussed in the previous sections. The classification of bioethanol fuel from different lignocellulosic materials and processes are currently being developed to meet sustainability and fuel quality standards, as well as the need for roads, aviation, and electricity. The processes of pretreatment, hydrolysis, and fermentation have significant effects on physico-chemical properties of bioethanol fuel, which also affect the internal combustion engines. The small changes in physico-chemical properties on bioethanol fuels are enough to create a significant change in the combustion system and sometimes make it difficult to analyze the fundamental of how it affects CO, CO_2, HC, NO_x and PM emissions. That means not all bioethanol fuel bring benefits to the environment concerning the emissions and performance. In the literature, the use of bioethanol as fuel goes back to the origin of the use of motorized vehicles. For example, Henry Ford's Model T, built in 1908, ran on bioethanol (Walter & Segerstedt, 2012). Interest waned in the following decades due to the environmental issue of reducing greenhouse gas, rising vehicle fuel demand, and the security of energy supply sustain the development of bioethanol production from renewable resources (Berhane, 2016; Purwadi, 2006; Yusuf & Inambao, 2019b)

Current research is focusing on how to blend bioethanol with gasoline or other additives under different ratios (Yusuf & Inambao, 2018) to take advantage of bioethanol high octane number and low cetane number, which increases thermal efficiency and compression ratios of the engine compared to gasoline alone (H. Zhao et al., 2011). Bioethanol provides additional oxygen in combustion; when blended with gasoline its burns relatively more completely, therefore emitting lower CO and HC emissions compared to pure gasoline (E0) (S. Liu, Cuty Clemente, Hu, & Wei, 2007; H. Zhao et al., 2011). The lower boiling point of bioethanol also helps to obtain better combustion efficiency (Hu, Wei, Liu, & Zhou, 2007). However, it has lower energy density than gasoline and lower vapor pressure (Balat, Balat, & Öz, 2008), and parts with lightweight design products directly influence the fuel consumption (Abdu, Shafii, Dubey, & Gupta, 2016). The properties of any fuel depend on it is a chemical composition

which determines the performance and emission characteristics of the engine. The properties of ethanol and gasoline are similar (as reported in Table 4).

Table 4 The physico-chemical properties of ethanol and gasoline

Properties	Units	Test Methods	Ethanol	Gasoline	References
Molecular formula	-	-	C_2H_5OH	$C_4 - C_{12}$	
Composition (C, H, O)	(Mass %)	ASTM D5291-02	52,13,35	86,14,0	(Mohebbi et al., 2018)
Density at 15 ℃	(Kg/L)	ISO 12185	0.79	0.73	(S. H. Park, Yoon, & Lee, 2014)
Boiling point	(℃)	-	78.3	27 to 225	(Hedfi, Jedli, Jbara, & Slimi, 2014)
Auto-ignition temperature	(℃)	-	360	228 to 470	(Balki, Sayin, & Canakci, 2014)
Flash point	(℃)	ASTM D93	21.1	-45 to -38	(H. Liu et al., 2014)
Lower hearting value	(MJ/kg)	ASTM D240	27.0	43.5	(Elfasakhany, 2016)
Octane number	VM	ASTM D2699	108	95	(Mařík, Pexa, Kotek, & Hönig, 2014)
Cetane number	-	ASTM D2700	11	0 to 10	(Rajesh Kumar & Saravanan, 2016)
Latent heat of vaporization	(KJ/kg)	-	838	223.2	(Thangavel et al., 2016)
Stoichiometric air/fuel ratio	w/w	-	9.0	14.7	(Gu et al., 2012)
Viscosity at 20 ℃	(mm²/s)	-	1.19	0.37 to 0.44	(Mohebbi et al., 2018; Yücesu, Topgül, Çinar, & Okur, 2006)
Saturation pressure at 38 ℃	(KPa)	-	13.8	31	(Thangavel et al., 2016)
Flammability Limit, 20 °C	(vol%)	-	3.3 to 19	1.0 to 8.0	(Ulrik, Troels, & Jesper, 2009)
Aromatics	(%v/v)	-	0	33.3	(Costagliola et al., 2016)
Enthalpy of formation Liquid Gas	(kJ/mol)	-	*-224.1* *-234.6*	*-259.28* *-277*	(Masum et al., 2013)

7. CONCLUSION

Bioethanol is an alternative fuel obtained from biomass and has been used in several countries for several years as it is considered to be renewable and clean energy. But not all bioethanol fuels bring benefits to the environment concerning the performance and emissions. Assessment needs to be made for each type of biomass material, location, and the extraction techniques.

According to the reviewed literature, both physical and biological processes are not cost competitive compared to the other pretreatments, but biological pretreatments are less harmful to the environment and can be performed in milder conditions, and thus are energy efficient compared to chemical and physico-chemical pretreatments. However, it is not possible to choose only one pretreatment as the best, because of the heterogeneity of the lignocellulose. The choice will depend on the nature or source of the lignocellulosic which needs to be treated, as well as on the use of the hydrolysate material. Fermentation processes have exhibited significant effects on bioethanol production. The SSF method has shown its ability to produce high ethanol concentrations with high productivity.

The processes of pretreatment, hydrolysis, and fermentation have significant effects on physico-chemical properties of bioethanol fuel, which also influence the internal combustion engines. The small changes in physico-chemical properties on bioethanol fuels are enough to create a significant change in the combustion system and sometimes make it difficult to analyze the fundamental of how it affects emissions.

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Chapter 3: Paper 2

Progress in alcohol-gasoline blends and their effects on the performance and emissions in SI engines under different operating conditions

This chapter highlights the progress in bioethanol-gasoline blends and their effects on the performance, emissions and some combustion characteristics in SI engines under different operating conditions. The article has been published in the *International Journal of Ambient Energy*, TAYLOR & FRANCIS Group.

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Progress in alcohol-gasoline blends and their effects on the performance and emissions in SI engines under different operating conditions

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ABSTRACT

Bio-alcohol has the potential to be used as an alternative to fossil fuels to reduce the total exhaust emissions from spark-ignition engines. This paper reviewed the most recent experimental studies on fundamental effects of performance, emissions and some combustion characteristics in SI engines. It also provides a guideline for suitable ethanol-gasoline and methanol-gasoline blend rates. Investigations were performed on different engines, operating conditions and rates of fuel blends with varying engine speeds. Most of the results showed that ethanol-gasoline has more benefits compared to methanol-gasoline in terms of exhaust emissions, engine power, and torque output, especially at low engine speed. The small differences in properties between ethanol-gasoline and methanol-gasoline blends are enough to create a significant change in the combustion system. These effects lead to behavioural mechanisms which are not easy to analyze or understand, sometimes make it difficult to identify the fundamentals of how ethanol or methanol affects emissions.

1. Introduction

Biofuels are a viable solution to end the global fossil fuel problems. The main environmental advantages of biofuels are their contribution towards reducing the level of SO_x, NO_x, CO_x, and CO_2 in the atmosphere. The energy consumption from transportation sectors has become a world problem. The world's energy demand is increasing every day and the problem of the fossil fuels depletion is becoming increasingly crucial. This problem led to new technologies in energy consumption management and the changing from conventional fuel to biofuels which are stringent necessity, both to meet the energy demands and to limit the production of carbon dioxides (Iodice and Senatore 2015, 2016). There is significant potential for agricultural involvement in the production and consumption of biomass energy. Biofuels are a variety of fuels which can be produced from biomass in many different ways. Alcohols are an important category of biofuels. Among the various alcohols, ethanol and methanol present the highest potential for use in the transportation sector mainly because they are cheap and have properties similar to gasoline (Agarwal, Karare, and Dhar 2014; Calam et al. 2015; Eyidogan et al. 2010; Koç et al. 2009). Alcohols have a high octane rating and high latent heat of vaporisation and oxygen in their molecular structure compared to gasoline, which leading to high efficiency of combustion and low emissions (Çelik, Özdalyan, and Alkan 2011). Ethanol and methanol have been extensively researched as alternatives to gasoline in internal combustion (IC) engines. Over the past century there have been significant improvements in conventional engine and fuel technology for improving performance (Maurya 2018). The utilisation of alternative fuel results in reducing the use of fossil fuels as well as increasing engine efficiency. Advancement in IC engine efficiency is still continuing; while much research has been conducted, not very much of it has been reviewed. Most researchers concentrate on how to replace gasoline with alternatives without considering the effects on the engine.

Ethanol (C_2H_5OH) is an ecological fuel, as it is obtained from renewable energy sources. It is a colourless, transparent, neutral, volatile, flammable, oxygenated liquid hydrocarbon, which has a pungent odour and a sharp burning taste (Abikusna et al. 2018; Ganguly, Chatterjee, and Dey 2012; Masum et al. 2013). The properties of ethanol and methanol are quite different (see Table 2). Ethanol has high flame speed, low stoichiometric air–fuel ratio and low heating value as compared to gasoline (Stone 2012).

Indeed, there are many investigations on ethanol-gasoline blends in gasoline engines. Ethanol–gasoline blends have several reported advantages, including an increase in engine torque, brake power and thermal efficiency (Bayraktar 2005; Najafi et al. 2009; Sileghem et al. 2013; Yoon et al. 2009; Yüksel and Yüksel 2004). Coskun et al. (2018) investigated the performance of a DI-HCCI engine at constant engine speed and high equivalence ratio conditions using different injection ratios (IR) of E10 and E20 blends. The results showed that the first injection variation does not have a significant effect on controlling homogeneous charge compression ignition (HCCI) combustion while the variation of the second injection timing and IR change peak pressure significantly. Costagliola et al. (2016) investigated the effect of ethanol-gasoline blends on a 4-stroke motorcycle. They

found that the engine showed power improvement with the addition of ethanol, the maximum improvement occurring at the range of ethanol 5% v–30% v gasoline fuel blend. Thangavel et al. (2016), Topgül et al. (2006) and Yücesu et al. (2006), used unleaded gasoline (E0) and unleaded gasoline-ethanol blends E10, E20, E40, E50, E60 and E85 in a single cylinder, four-stroke, spark-ignition engine under different compression ratio. They found that blending unleaded gasoline with ethanol slightly increased the brake torque and decreased carbon monoxide (CO) and hydrocarbon (HC) emissions. The authors also concluded that blending with ethanol allows increasing the compression ratio without knock occurrence. Turner et al. (2013) studied the effects of ethanol–methanol–gasoline blends on sperk-ignition (SI) engine emissions using five different rates from 30% v to 42% v gasoline and from 58% v to 70% v ethanol–methanol. The results showed that the dual fuel blends have reduced carbon dioxide (CO_2) and nitric oxides (NO_x) emissions, compared to the neat gasoline.

A very important aspect of using blended fuels in spark-ignition engines is the change in properties. Davis and Heil (2000) compared the performance of four alcohols and found that the charge density increased when using alcohol because of the evaporative cooling in the intake manifold. Hara and Tanoue (2006), Beeckmann, Röhl, and Peters (2009) and Farrell, Johnston, and Androulakis (2004) reported that ethanol has a higher laminar flame velocity than that of gasoline/iso-octane. However, Da Silva et al. (2005) concluded that ethanol up to 25% by volume in gasoline led to an increase in reid vapour pressure and octane ratings. Similar results were found by Kar et al. (2008), namely, that the addition of ethanol to gasoline causes a non-linear change in the vapour pressure of the resulting mixtures using the methods listed in Table 1. Although ethanol has a lower vapour pressure than gasoline, as the ethanol content is increased up to 30% of the vapour pressure increases, but further ethanol addition then causes a reduction in vapour pressure. This phenomenon causes the maximum cooling effect to be seen for approximately 50% ethanol content due to the competing factors of increasing enthalpy of vaporisation (low blends) and reducing vaporisation (lower vapour pressure for high blends). Iodice and Senatore (2013) reported that the Reid Vapor Pressure (RVP) of ethanol is very lower than that of gasoline, the resulting lower volatility of ethanol can cause difficult cold transient of the engine during the warm-up phase. Nevertheless, with the growth of ethanol content, at first, the RVP of the blended fuel rises to reach a maximal value at about 15% v/v of ethanol addition (so facilitating the cold-start). Therefore, at higher ethanol percentages, the RVP declines.

Richards (1995) described an improvement of 16% on the performance of a single-cylinder, ethanol-fuelled engine when the compression ratio was increased from 8 to 18.

Methanol (CH_3OH), which is also called methyl alcohol, is a colourless, pure substance, and is simplest form of saturated alcohol. Methanol can be produced from biomass, natural gas, or coal (Clausen, Houbak, and Elmegaard 2010; Holmgren et al. 2012; Kumabe et al. 2008; Li et al. 2010; Renó et al. 2011), and can be used in low-cost IC engines with only minor adjustments to ensure material compatibility. Many studies have been conducted on methanol-gasoline blends under different ratios or volumes. Abu-Zaid, Badran, and Yamin (2004) investigated the performance of M3, M6, M9, M12 and M15 fuel blends and found the maximum power output with the M15 fuel blend. Hu et al. (2007) studied the addition of methanol in gasoline. Results showed that the methanol reduces the phase of rapid burning and advances the start of combustion. The maximum pressure of the blends was high compared to gasoline. Iliev (2015) analyzed the performance and emissions characteristics for different blends of ethanol, methanol, and gasoline using a 1-D engine model. Results showed that the brake power (BP) decreased and the brake specific fuel consumption (BSFC) increased when using alcohol-gasoline fuel blends. As the fuel blend proportions increased to E30M30, the NO_x emissions increased with a decrease in the CO and HC concentration. Methanol can be blended with gasoline fuel, which can improve engine performance such as power, fuel economy, and emissions (Canakci et al. 2013; Çay et al. 2013; Gravalos et al. 2013; Siwale et al. 2014). For instance, methanol can suppress knocking combustion (Liu, Wang, and Wang 2014); decrease HC, CO, PM, and NOx emissions; and improve thermal efficiency (Liang et al. 2013; Wu et al. 2016).

Some researchers have studied the effects of methanol-gasoline blends using a different approach. Liao et al. (2006) studied the effects of methanol-gasoline blends on combustion characteristics at relatively low temperatures. They found that the HC emissions during the rich mixture combustion increased with additional methanol in the methanol-gasoline blends at relatively low temperatures, due to the increase in evaporation heat absorbed by the blended fuel compared to gasoline. Yanju et al. (2008) analyzed the effect of methanol blends in IC engines, and the results showed that for M85 there was a reduction of emissions of CO and NOx by 23% and 80% respectively. Gong et al. (2011) investigated the effects of ambient temperature on the firing behaviour and the unregulated emissions of electronically controlled inlet port injection spark-ignition methanol. The test results indicated that the minimum amount of methanol injected per cycle to ensure the methanol engine reliable firing increases 86% with the reduction of the ambient temperature from 301 K to 289 K. Wang et al. (2016) evaluated the effects of engine misfire on regulated and unregulated emissions from methanol fuelled engine, and the results showed that the unburned methanol emission increased by least 1.6 and 5.7 times for misfire rates of 6% and 9%, respectively.

This review paper aims to study the experimental effects of various fuel blends such as ethanol–gasoline and methanol–gasoline on engine performance and emission characteristics under different modes of operation. The purpose of selecting various blend ratios within a certain interval is to design based on environmental friendly and obtain the best emission levels.

Table 1. Emission measurement method using the Horiba MEXA-7100DEGR gas analyzer.

Emission	Measurement method
HC	FID (hot)
CO	NDIR (dry)
CO_2	NDIR (dry)
NO_x	CLD (dry)

2. Experimental overview

2.1. Engines

In this section, experiments and procedures with various engines are reviewed, namely: 1-cylinder, 2-stroke SI engines; 4-cylinder, 4-stroke SI engines; 4-cylinder, 8-valve SI engines; 1-cylinder, modernised spark-ignited direct injection (SIDI) SI engines; port fuel ignition engines; and 4-cylinder, electronic fuel injection, ECA engines. Isermann (2014) explained the historical modifications of gasoline or SI engines during the last 50 years with view on their control and diagnosis. Modifications for the improvement of gasoline engines include, for example, variable valve trains, downsizing, and modified combustion processes. Variable valve trains (VVT: variable valve timing) permit the improvement of the gas exchange (Grasreiner 2012; Isermann 2017; Köhler and Flierl 2011; Yang 2011). There are various designs of VVT. Schulz, Kulzer, and Vollmer (2006) found that fuel consumption can be improved with a continuously variable lift by 8%–10%, phase actuation by 3%–4%, lift switching by 8%–10%, and with full variable hydraulic or electrical VVT by 14%–16%.

2.2. Test procedure

After preparing the fuel blends such as ethanol–gasoline and methanol–gasoline at different ratio, the performance of each blend were tested in IC engines. The quality of any fuel depends fully on its physical and chemical properties which determine the performance, emission characteristics and engine combustion. Table 2 shows the comparison of gasoline, ethanol, and methanol as fuel when related to combustion. To analyze the combustion process of the IC engine, a pressure transducer can be used to measure pressure cycles at different steady-state conditions. According to the reviewed papers, the engines were instrumented with various instruments for testing the engine parameters such as brake thermal efficiency, brake power, brake specific fuel efficiency, volumetric efficiency and torque output; and pollutant emissions such as CO, CO_2, NO_X, and HC. The engine speeds were controlled by an engine dynamometer both at constant engine speeds and variable engine speed intervals. The experimental results of the various engine combustion characteristics, performance, and emission parameters are discussed separately in the next section. This overview focuses on analysis. Detailed information with thorough descriptions of the experimental setup and procedure can be found in the relevant publications (Aulich et al. 1994; Costagliola et al. 2013; Dai et al. 2013; Gong et al. 2017; Huang and Hong 2016; Li et al. 2015; Poran and Tartakovsky 2017; Sakai and Rothamer 2017; Sileghem et al. 2012; Turner et al. 2011; Wang, Chen, et al. 2015; Wang, Liu, et al. 2015).

3. Results and discussion

3.1. Engine performance characteristics

3.1.1. Brake specific fuel consumption (BSFC)

3.1.1.1. Effect of ethanol-gasoline blends on BSFC. Eyidogan et al. (2010) carried out an experiment which showed the comparison of BSFC for ethanol blend fuels at different vehicle speeds (80 km/h and 100 km/h). The experimental results showed that the BSFC at both speeds increased by a certain percentage. It was observed that BSFC for M5 was lower than that of E5 and for M10 was lower than that of E10. This is due to the content of oxygen which causes combustion efficiency to increase or decrease in BSFC. There is an increase in BSFC when the mixing ratio of ethanol is higher, therefore E10 provided the lowest BSFC. These results show a similar trend to the studies conducted by (Balki and Sayin 2014; Celik 2008; Gravalos et al. 2011; Phuangwongtrakul et al. 2016). A study by (Najafi et al. 2009) showed the relationship between BSFC and engine speed for different fuel blends. The results showed that the BSFC decreases as the ethanol ratio increases. As engine speed increases reaching 3500 rpm, the BSFC decreases reaching its minimum values. This is due to the increase in brake thermal efficiency. However, the increase in bioethanol ratio will result in higher specific fuel consumption compared to pure gasoline. This trend is due to the lower calorific value of bioethanol compared to gasoline

(Al-Hasan 2003). investigated the effect of torque, volumetric, brake power and brake thermal efficiencies in an SI engine. Results showed that the BSFC and equivalence air–fuel ratio decreased, and fuel consumption showed a marginal increase with ethanol-gasoline blends. This effect is due to the increase in brake thermal efficiency and a decrease in equivalent air–fuel ratio. However, an increase in engine speed results in increasing BSFC, since the brake thermal efficiency decreases and the equivalent air–fuel ratio increases. The authors concluded that E20 gave the best results at all engine speeds.

Table 2. The physical and chemical properties of Gasoline, Ethanol, and Methanol.

Property	Units	Gasoline	Ethanol	Methanol	References
Molecular formula	–	C_4–C_{12}	C_2H_5OH	CH_3OH	
Composition (C, H, O)	Mass %	86, 14, 0	52, 13, 3	37, 12.5, 50	Mohebbi et al. (2018)
Lower hearting value	MJ/kg	43.5	27.0	20.1	Elfasakhany (2016)
Density	Kg/m^3	737	785	792	Agarwal (2007)
Octane number	VM	95	108	109	Mařík et al. (2014)
Cetane number	–	0–10	11	2	Kumar and Saravanan (2016)
Heat of vaporisation	KJ/kg	223.2	838	1100	Thangavel et al. (2016)
Boiling point	°C	25–215	78–79	64–65	Brown (2008), Hedfi et al. (2014)
Auto-ignition temperature	°C	257	423	463	Kumar et al. (2013)
Flash point	°C	45 to −38	21.1	11.1	Liu et al. (2014)
Stoichiometric air/fuel ration	w/w	14.7	9.0	6.4	El-faroug et al. (2016), Thangavel et al. (2016)
Viscosity at 20°C	mm^2/s	0.37–0.44	1.19	0.58	Elfasakhany (2016)
Saturation pressure at 38°C	KPa	31	13.8	31.68	El-faroug et al. (2016)
Laminar flame speed	cm/s	∼ 33	∼ 39	–	Gu et al. (2012)

Phuangwongtrakul et al. (2016) experimentally determined the optimal blend rate of ethanol-gasoline in order to maximise the performance characteristics of a commercial SI engine. This experiment was conducted at various engine speeds and percentages of the intake-throttle opening using constant compression ratio. A contour plot was drawn for the corresponding BSFC according to the relevant ethanol composition at the specified throttle positions and engine speeds. The BSFC is relatively high for low engine speed. The engine seems to operate at the lowest BSFC around 65%–85% WOT while supplied with 40% composition by volume of ethanol in gasoline. The curve fitted relations for the corresponding BSFC according to relevant ethanol composition at various percent WOT.

3.1.1.2. Effect of methanol-gasoline blends on BSFC.
Fu et al. (2014) carried out a study on how to improve fuel efficiency and achieve the goal of direct usage of methanol fuel on an IC engine. At brake mean effective pressure (BMEP) (3 and 6 bar) using two different IC engines, it was found that with methanol vapour fuel, the equivalent BSFC of the IC engine was reduced significantly compared to a gasoline engine. Moreover, at the brake mean effective pressure of 3 bar, it decreased but not more than 92.5 g/(kWh). The equivalent BSFC of a dissociated methanol fuelled engine was slightly lower than that of the methanol vapour fuelled engine. This shows that exhaust heat dissociating methanol fuel is a useful way to enhance IC engine thermal efficiency. Therefore, when there is an increase in methanol dissociation rate (from methanol vapour to methanol dissociation gas), the energy saving potential of the IC engine becomes higher. This is due to the net calorific value of a fuel which is further added.

Abu-Zaid, Badran, and Yamin (2004) investigated the effect of addition of methanol to gasoline on the performance of SI engines. Performance tests were carried out at wide open throttle (WOT) under variable speed conditions, using various fuel blends of methanol-gasoline. The results showed that the BSFC was inversely proportional to the thermal efficiency and calorific value of the blend. The calorific value of the blend decreased as the percentage of methanol increased. However, at low engine speed (from 1000 rpm to 2500 rpm), the effect of a decrease in BSFC seemed to be the most influential factor. This may explain that the lowest BSFC at these speeds was for pure gasoline, which agrees with the experimental studies conducted by Al-Hasan (2003) and Gravalos et al. (2011). A similar result was obtained by Agarwal, Karare, and Dhar (2014) who carried out experimental research on methanol blends which showed the variations of BSFC with engine load (BMEP) under different engine speeds. These indicate that the BSFC for methanol blends was high at some engine operating conditions, due to the relatively lower heating value of methanol compared to gasoline and it did not contribute to heat generation during in-cylinder combustion.

3.1.2. Brake thermal efficiency
3.1.2.1. Effect of ethanol-gasoline blends on brake thermal efficiency.
Ananda and Saravanan (2013) carried out an experiment on emission reduction for ethanol-gasoline blends using fuel additives in an SI engine. The final results showed an increase in the brake thermal efficiency at different ethanol

blends in a multi-cylinder petrol engine. The engine performance improved when additives were used with the ethanol-gasoline blend in the calculated percentage named as sample one (E50 + 10% of additives) and sample two (E60 + 10% of additive). However, sample two generated the best results compared to sample one, and operating at 2800 rpm the brake thermal efficiency was found to be 23.24%. Al-Hasan (2003) showed the effect of using unleaded gasoline-ethanol blends on brake thermal efficiency. Brake thermal efficiency increased as the percentage of ethanol increased. The maximum brake thermal efficiency was recorded when the percentage of ethanol in the fuel blend was at 20% for all engine speeds.

Wang et al. (2018) showed the breakdown of thermal efficiency gains for ethanol-gasoline blends in TC DISI engines. Results showed that the engine thermal efficiency gains were affected mainly due to a cooling effect and chemical effect, both of which increased with the ethanol ratio. These results pointed out that the chemical effect is the most dominant, especially for the blend with a low research octane number (RON) base fuel. Also, the cooling effect shows a significant effect for the blend with a low RON94.5 ($\Delta EOI/\Delta CR = 4$) base fuel. However, the improvement of engine downsizing, flame speed effect, and octane sensitivity were comparable and were less than those of chemical and cooling effects. With a little amount of ethanol addition, the engine thermal efficiency increased faster than the reduction of lower heating value (LHV). When the ethanol content was high the thermal efficiency decreased. This trend was reported by other researchers as well (Jo, Bromberg, and Heywood 2016; Leone et al. 2015; Liu et al. 2015; Wang, Janssen, et al. 2017; Wang, Zeraati-Rezaei, et al. 2017), who suggested that for compression ratios from 8:1 to 14:1, the thermal efficiency gain with compression ratio is almost linear ($\Delta\eta/\Delta CR = 1.8\%$). The contribution of the high flame speed of ethanol to thermal efficiency is 0.20% for every 10% by volume of ethanol content in fuel blends. They emphasised that engine downsizing is a technology that increases engine thermal efficiency by allowing an engine to operate at more efficient high load regimes, instead of at low load regimes where pumping losses significantly reduce engine thermal efficiencies. The researchers suggested that a thermal efficiency increment multiplier from additional engine downsizing for TC DISI engines.

3.1.2.2. Effect of methanol-gasoline blends on brake thermal efficiency (BTE).
Murali Krishna et al. (2012) showed the impact of two different engines (copper coated engine CCE and conventional engine CE) using methanol blended gasoline at a compression ratio (CR) of 7.5:1 and speed of 3000 rpm. They found that the BTE increased up to 80% of a full load and beyond that load; it decreased with an increase of BMEP for two different engines with test blend fuels. Higher BTE was observed with methanol-gasoline blended fuel compared to gasoline at all loads due to the lower stoichiometric air requirements of methanol blended gasoline. The copper coated engine showed higher thermal efficiency when compared to a conventional engine with both test fuels at loads, particularly at near full load operation. Liu et al. (2007) investigated the effect of using methanol blends (M10, M15, M20, M25 and M30) on SI engines under full load conditions. They found that both engine power

and torque decreases, while the BTE improved with higher percentages of methanol blend.

Yanju et al. (2008) conducted a study on three different methanol-gasoline blends (M10, M20, and M85) to investigate the effect on engine power, thermal efficiency, and emission characteristics. It was found that the addition of methanol significantly improved the BTE. These occur when the laminar flame speed is high, which increases the thermal efficiency by completing the combustion earlier which decreases heat losses from the cylinder. However, methanol exhaust contains lower concentrations of particulate matters and nitrogen oxides than gasoline exhaust (Heywood 1988; Hinze and Cheng 1993; Zhang et al. 2007). A study by Çelik, Özdalyan, and Alkan (2011) showed the effect of methanol-gasoline fuels on brake thermal efficiency at various CRs and engine speeds. Results showed that the values of BTE obtained with methanol were about 22.1%, 27.3% and 30.3% at CRs of 6:1, 8:1 and 10:1, respectively. Also, for gasoline is 19.2% at CR of 6:1. However, the brake thermal efficiency of methanol is about 16% higher than that with gasoline at the same CR (6:1).

3.1.3. Brake power
3.1.3.1. Effect of ethanol-gasoline blends on brake power.
Tibaquir et al. (2018) studied analytically and experimentally the effects of using low ethanol content ($< 20\%$ v/v) in the mechanical and environmental performance of in-use sedan-type gasoline fuelled vehicles, without any modifications of the engine. When 20% of ethanol is used instead of gasoline, the power generated by the engine decreases from 0.19% to 0.48% depending on λ (relative air/fuel ratio). This decrease can be up to 2.6% when using E85 at constant speed 5000 rpm. These significant changes in power result from the effect generated by the reduction in the air/fuel ratio (A/F 20% of Ethanol = 13.31 vs. A/F Gasoline = 14.49) to the negative effect of the lower energy content of the ethanol (LHV 20% of Ethanol = 39,860 kJ/kg vs. LHV Gasoline = 43,370 kJ/kg). The engine requires less air to burn the same mass of fuel, and therefore it can increase the amount of fuel injected into the combustion chamber per engine cycle, which increases the power generated during each cycle. When the engine operates with E20, it uses a fuel with 8% less energy content than when it operates with gasoline, but it can use 8.1% more fuel. The net effect is a minor reduction in power is ($< 0.2\%$ for $\lambda = 1$).

Doğan et al. (2017) measured the best effective engine power at E0, E10, E20 and E30 fuels in various test speeds. They analyzed that when there are lower thermal values of blend fuels compared to gasoline; then there will be a decrease in torque which affects the performance of the engine power. Results showed that for all the fuels that in the effective power measured due to the increase engine speeds, it was determined the engine power increased according to the amount of work per unit time. They measured the highest effective power was 37.23 kW at 4500 rpm for the E0 fuel while the lowest effective power was 18.08 kW for E30 fuel.

Research by Najafi et al. (2015) showed the effect of different fuel blends at different engine speeds on brake power. Results showed that when the bioethanol content increased, the engine brake power slightly increased for all engine speeds. The increment in engine power contributed toward an increase

in indicated mean effective pressure when the ethanol content blends were high. They observed that the heat of evaporation in ethanol is higher than that of gasoline, which provides the fuel–air charge cooling and increases the density of the charge. They also suggested that when the ethanol content is increased, the engine volumetric efficiency and the density of the mixture increases while decreasing its heating value, thus increasing torque and power.

3.1.3.2. Effect of methanol-gasoline blends on brake power.
Divakar Shetty and Antony (2017) investigated experimentally the effects of methanol-gasoline blends on engine performance and combustion characteristics using a 4-stroke cylinder digital twin spark ignition engine. The tests were performed at various loads at M10, M15, M20, M25, M30 and pure gasoline also at 32° BTDC for one spark plug and 28° BTDC for the other one. The results showed that the power obtained with gasoline was 1.22 KW at maximum load. However, the power obtained varied from 1.62 KW to 2 KW depending on the blend. The engine power was increased by 13% at minimum load. One of the reasons for the increase in power by methanol blend fuels is that methanol has a high laminar flame speed compared to gasoline and this helps to complete the combustion process before heat losses from the cylinder (Heywood 1988; Hinze and Cheng 1993). As the torque increases, the power also increases.

3.1.4. Torque output
3.1.4.1. Effect of ethanol-gasoline blends on torque output.
Najafi et al. (2015) carried out studied the performance parameters and exhaust emissions of an SI engine operating with ethanol-gasoline blends of 5%, 7.5%, 10%, 12.5% and 15%. In the experiments, the engine ran at various speeds for each test fuel and 45 different conditions. The results showed that at optimal input parameters, the values of the performance were found to be close to gasoline, and emission characteristics of the engine improved significantly. They also investigated the effect of various test fuels on torque at different engine speeds. When the content of bioethanol blend fuel increased, the engine torque slightly increased for all engine speeds. This is due to fuel–air charge cooling which increases the density of the charge since the heat evaporation for gasoline is lower than that of ethanol and thus higher torque output and power is obtained.

Doğan et al. (2017) investigated the engine performance and exhaust emissions of ethanol-gasoline blends through exergy analysis with a 4-cylinder, 4-stroke SI engine. The experimental results showed that the maximum value of engine torque measurements was obtained between 2500 rpm and 2750 rpm for all fuel types and the lowest value was measured in 4500 rpm with E30 fuel. Additionally, the engine torque decreased by approximately 2% for E10, 3% for E20 and 5% for E30 compared to gasoline. The observation was made that when the ethanol ratio is added to the gasoline, the difficulty in starting the engine increases, and when the engine speed is higher than 4000 rpm, the engine works less regularly.

Serdar Yücesu et al. (2007) carried out an experimental analysis of SI engine performance using ethanol-gasoline blend fuel (E0, E10, E20, E40, and E60). The experiments were performed by varying the ignition timing, relative air–fuel ratio (RAFR), compression ratio at a constant speed of 2000 rpm and wide open

throttle (WOT), which are all parameter which affect the engine. The results showed the effects of ignition timing on brake torque and BSFC at the compression ratio of 10:1. It was found that the maximum brake torque was obtained at 22 CA (crank angles) advanced ignition timing with all fuels. When the ignition timing was increased to 24 CA, a knock occurrence was observed with E0 fuel. It was also observed that there was no-knock occurrence at 36 CA advanced ignition timing with unleaded gasoline-ethanol blends (E40 and E60). However, using ethanol-gasoline blends increased the compression ratio without knock occurrence in SI engines for better thermal efficiency, and increased the brake torque and BSFC at all ignition timings. They concluded that ethanol blends could serve as agents to raise the octane number of gasoline and be used as an anti-knock additive to unleaded gasoline.

Costa and Sodré (2010) compared the performance and emissions from a production 1.0-l, eight-valve, and four-stroke engine fuelled by hydrous ethanol at 6.8% of water content and 78% gasoline-22% ethanol blend. The results showed a significant increase in torque and BMEP at speeds below 3250 rev/min when the gasoline-ethanol blend was used as fuel. When the speeds were above 4000 rev/min, the hydrous ethanol produced higher torque and BMEP. At low engine speeds, the higher heating value of gasoline was responsible for the higher torque and BMEP obtained for the gasoline-ethanol blend (see Table 2). At high engine speeds, the faster flame speed together with increased ignition timing enabled hydrous ethanol to produce higher torque and BMEP than the gasoline-ethanol blend. Also, these generate less time to complete combustion in an engine cycle, and a faster flame velocity is required. This flame speed is affected by several parameters, such as pressure, mixture temperature and air/fuel mixture (Sodré 1998).

3.1.4.2. Effect of methanol-gasoline blends on torque output.
Balki, Sayin, and Canakci (2014) conducted an experimental study on the effect of ethanol and methanol use on the performance, emissions and combustion characteristics of a low power single-cylinder engine. The tests were conducted at full-throttle valve opening and variable engine speeds. Results showed changes in engine torque and BSFC at various engine speeds for the three different fuels. Maximum torque was obtained at 2400 rpm. On average, the maximum engine torque for pure methanol and ethanol increased by 4.7% and 3.7% respectively, when compared to gasoline. The best value of the engine torque obtained with methanol was 11.76 Nm. Engine torque reduced after it reached the maximum point along with the increase in engine speeds. However, the decrease in torque while using gasoline was higher than that of alcohol fuels.

Kapusuz, Ozcan, and Yamin (2015) carried out an investigation on different alcohol-unleaded gasoline mixtures used in a SI engine without any modifications. The fuel blend ratios were from 5% to 15% of ethanol and methanol together and separately, and were optimised using artificial neural network. The simulated result was obtained from the ANN model then afterwards taken for further analysis at 1400 rpm. The alcohol content at maximum torque speed for the different mixtures was obtained. This showed that the torque decreased when the ethanol ratio was 6%. The lowest torque value was obtained with the mixture of ethanol 7% and methanol 8%. The maximum torque value was obtained when the ethanol ratio was 1% and the methanol ratio was 11%.

Qi et al. (2005) studied the effect of ethanol as a co-solvent in a methanol-gasoline blend in an SI engine. The critical phase separation temperature (CPST) of the methanol-gasoline blend increased with an increase in water content in the blend, but adding the ethanol content caused the CPST to decrease. The results showed that the higher the volume fraction of methanol in the blend, the larger the reduction. Also, when the fuel consumption per stroke of gasoline was larger than that of M25, this caused the air-M25 ratio to increase with a consequent decrease in the heating value of the mixture. When there was an increase in excess air coefficient, there was a resulting loss of power. This means that the torque output of various blends was lower than that of gasoline at all engine speeds.

3.2. Engine emission characteristics

3.2.1. CO emission
3.2.1.1. Effect of ethanol-gasoline blends on CO emission.
According to reviewed literature, different studies have indicated that the oxygen content in ethanol result in a significant reduction in CO emission. But the percentages of reduction reported by different researchers are not the same. Hsieh et al. (2002) conducted an experimental investigation on engine performance and pollutant emission of a commercial SI engine using different ethanol-gasoline blend fuels (0%, 5%, 10%, 20%, and 30%) at engine speed of 3000 rpm. Results showed that with increasing the ethanol content, the Reid vapour pressure of the blended fuels initially increased to a maximum at 10% ethanol addition, and then decreased. The researchers also found that the reduction of CO emission grows as the ethanol content increases. Kiani et al. (2010) investigated the performance of the ANN validation by comparing the prediction dataset with the experimental results and found that the ANN provided the best accuracy in modelling the emission indices with correlation coefficient. They concluded that the experimental results confirmed that by adding more ethanol, the CO was decreased.

Jin et al. (2017) investigated the effects of various ethanol-gasoline blends on the hazardous air pollutants (HAPs) emissions using the federal test procedure (FTP-75) mode. The CO emissions showed a decreasing trend as the ethanol proportion in the fuel increased. CO emissions with E0 and E85 were reduced from 0.275 g/km to 0.147 g/km under the FTP-75 mode. Incomplete combustion of the air–fuel mixture during cold transient operation and fuel-rich environment stages produced significant CO emissions.

Hsieh et al. (2002) studied the performance and exhaust emissions using an SI engine fuelled with ethanol–methanol-gasoline blends. The test results obtained at low content rates from (3– 10 vol.%) in gasoline were compared to ethanol-gasoline blends, methanol-gasoline blends, and pure gasoline test results. Also, decreases in CO emissions took place with the increase in vehicle speed for all test fuels. In the case of EM blends, for example at 2600 r/min, the CO emission was about 13%, on average, compared to neat gasoline. Therefore, at 3450 r/min, the CO emission for the same fuel becomes about 35%. These results showed that the addition of ethanol or methanol into gasoline is more efficient for getting lower

emissions at high engine speeds (> 3000 r/min). However, methanol-gasoline blends presented the lowest emissions of CO among all test fuels.

A study by Saikrishnan, Karthikeyan, and Jayaprabakar (2018) which depicted the effect of ethanol-gasoline blends on CO emission against torque. CO is a product of incomplete combustion due to insufficient air content in the air–fuel mixture. The researchers showed that when ethanol contains oxygen and then is mixed with gasoline, the combustion of the engine becomes better, and the CO emission decreases. Thus, the concentration of HC and CO decreased as the volume percentage of ethanol blend fuel increased. This result is due to the reduction in carbon atoms concentration in the mixed fuel and the high molecular diffusivity and high flammability limit which improve the mixing process and hence combustion efficiency.

3.2.1.2. Effect of methanol-gasoline blends on CO emission.
Alexandru, Ilie, and Dragos (2017) carried out research on the variation of pollutant emissions versus the load of the engine at different engine speeds of 3600 rpm and 4600 rpm using an SI engine. The results showed that the values of CO decreased once the ratio of methanol increased. The researchers stated that such an effect is due to the quantity of oxygen contained by the alcohol, and because the carbon content gasoline is greater than in methanol.

Aulich et al. (1994) found that the CO emissions trend obviously decreased with the content of methanol fuel and depended mainly on the excess air ratio. At M25, the CO emissions decreased by certain percentages at all loads compared with those of gasoline. During combustion, it was observed that methanol fuel has oxygen that produces some radicals such as OH and O with strong oxidation.

Xie et al. (2013) studied the performance and emission characteristics using exhaust gas recirculation (EGR) and spark timing to control a load of SI methanol with WOT. The experimental results showed that at an engine speed of 1400 rpm and full load, the methanol ran stably without knocking, specifically when the ignition timings were 18 CA, 15 CA and 12 CA (crank angle) BTDC. Their study also indicated that the CO emissions of the control method using EGR and ignition timing were decreased at higher engine loads. At lower engine loads, CO obviously deteriorated and were 3–4 times higher than those of the conventional control method. Therefore, better performance and lower emissions can be achieved by a control method using EGR and ignition timing when the engine load is higher.

3.2.2. CO$_2$ emission
3.2.2.1. Effect of ethanol-gasoline blends on CO$_2$ emission.
Iodice, Langella, and Amoresano (2017) evaluated the influence of the addition of ethanol in gasoline fuel blends on energy consumption and exhaust emissions during the warm-up phase and cold-start transient of current generation SI engines. The CO$_2$ emissions were measured within the cold and hot phases of the European type-approval driving cycle. The results showed that the CO$_2$ emissions in the cold phase were decreased with the addition of ethanol in the blends.

Saikrishnan, Karthikeyan, and Jayaprabakar (2018) conducted research on a three-cylinder, four-stroke SI engine at constant speed with different percentages of ethanol as the additive to gasoline. Results showed that CO$_2$ increased compared to pure gasoline fuel for various ethanol blends. The opposite behaviour was observed with CO emissions which improved as the percentage of ethanol increased, because of the improved combustion process as a result of the oxygen content in the ethanol fuel.

Jin et al. (2017) studied the effects of various ethanol-gasoline blends (E0, E10, E30, E50, and E85) on the hazardous air pollutants (HAPs) emissions in a SIDI engine. As the content of ethanol increased in the gasoline fuel, the CO$_2$ emissions decreased significantly. The CO$_2$ emissions and fuel economy (FE) with various ethanol ratios were measured to be 190 g/km (E0), 189 g/km (E10), 187 g/km (E30), 188 g/km, and 187 g/km (E85) and 12.3 km/L (E0), 11.9 km/L (E10), 11.2 km/L (E30), 10.2 km/L s(E50), and 8.7 km/L (E85). The results indicated that the 1.6% ethanol ratio reduced the CO$_2$ emissions from E85 fuel compared to gasoline. This is due to the lower heating value of ethanol fuel. They suggested that more fuel injection from ethanol fuel is needed to compensate for decreases in engine performance. Thus, the FE of ethanol content fuels was slightly reduced by 3.3% (E10), 8.9% (E30), 17.1% (E50), and 29.3% (E85).

3.2.2.2. Effect of methanol-gasoline blends on CO$_2$ emission.
CO$_2$ is non-toxic emission but leads to the greenhouse effect. Research conducted by Çelik, Özdalyan, and Alkan (2011) studied the effect of methanol-gasoline on CO$_2$ at various CRs and speeds. The results indicated that CO$_2$ is lower than that of gasoline at all CRs with methanol added. At the same CR = 6:1 with methanol, CO$_2$ is about 37% lower than that of gasoline. CO$_2$ emission obtained with methanol at the CR of 10:1 is about 30% lower than that with gasoline at the CR of 6:1. These research results are similar those that of Celik and Colak 2008; Wu et al. (2004).

A recent experimental investigation by Divakar Shetty and Antony (2017) investigated the effect of gasoline and methanol blend fuels using an SI engine at various loads. The results showed that the CO$_2$ emission increased with an increase in load but decreased when the methanol content in the blend increased. At maximum load, the CO$_2$ emissions decreased at about 17% at maximum load. According to the literature, the emission of CO$_2$ mainly depends on the C–H ratio in the fuel. This result is due to less C–H ratio and C content in methanol which shows less CO$_2$ emission compared to gasoline (Ozsezen et al. 2009; Pourkhesalian, Shamekhi, and Salimi 2010; Turns 2000).

3.2.3. NO$_x$ emission
3.2.3.1. Effect of ethanol-gasoline blends on NO$_x$ emission.
Previous literature (Hsieh et al. 2002; Stump, Knapp, and Ray 1996) have found some increment in NO$_x$ emission for ethanol. A different trend was observed by other researchers (Furey and King 1980; Lapuerta et al. 2005; Rice et al. 2016). Some researchers (Lapuerta, Armas, and Herreros 2008; Tavares et al. 2011) investigated the irregularity in NO$_x$ emission with ethanol. In this section the causes of NO$_x$ emission will be discussed for ethanol-gasoline blends; attention will be given to various fuel blends, various vehicle conditions, various engine parameters and as well as engine modifications.

Najafi et al. (2009) found that the oxygen content of ethanol produces a slight effect in fuel-rich conditions. This slight effect shifts the air–fuel ratio to stoichiometric conditions and helps

in completing combustion, although this increases NO_x emissions. Another similar study by Masum et al. (2015) examines the variation in NO_x emission at WOT and different engine speeds. They found that on average, NO_x emissions increased more on ethanol compared to gasoline. Schifter et al. (2013) conducted a study on both anhydrous and hydrated ethanol, and found that for hydrated ethanol, the emission decreased as the oxygenate contents increased. Regarding anhydrous ethanol, the NO_x increased when the ethanol content was 30% and higher.

Zhuang and Hong (2013) mixed ethanol-gasoline blends from 0% to 60.1%. Results showed that NO_x emission increased up to 24.3% ethanol to gasoline after which it decreased with further increases in ethanol percentage. They showed that a higher percentage of ethanol in gasoline reduces NO_x as well as in-cylinder temperature. Other research on ethanol-gasoline blends of 30% (Chen et al. 2010) and 50% (Agarwal 2007) compared to gasoline (Li et al. 2003; Niven 2005; Poulopoulos, Samaras, and Philippopoulos 2001) also found that NO_x emissions reduced. Ananda and Saravanan (2013) studied the effect of unleaded gasoline–ethanol blends on NO_x emissions and found that NO_x emissions were significantly reduced for all engine speeds for sample two compared to the other samples. Further, results showed that the blends decreased the combustion temperature in the cylinder and lowered the combustion heat energy.

Koç et al. (2009) demonstrated that the NO_x emissions of ethanol-gasoline blends (E50 and E85) were lower than that of gasoline at different compression ratios (CR = 10:1 and CR = 11:1). The NO_x emissions at CR = 11:1 were slightly higher than that of CR = 10:1 in all speed ranges. It was concluded that when the latent heat of vaporisation is high and with low flame temperature, then the NO_x emission will be low. But, the NO_x emission may change depending o on the ratio of ethanol in the blend and operating conditions.

3.2.3.2. Effect of methanol-gasoline blends on NOx emission.
Aulich et al. (1994) conducted an experimental study on a non-road small gasoline engine using pure gasoline and methanol-gasoline blend fuels (M15 and M25). The results showed that the NO_x emissions increased when the methanol ratio increased. With increased engine load, the NO_x emission for gasoline increased, as did the NOx emissions for the blends. When the engine load was at 75%, M15 and M25 showed peak values of 550.4 ppm and 964.3 ppm, respectively. This suggests that there is complete combustion at 75% load and the cylinder gas temperature is higher, compared with other loads.

Vancoillie et al. (2013) compared the engine-out NO_x emissions on methanol and gasoline at various fixed loads. The estimated uncertainty was below 1 g/kWh for all measurement points. The values were consistently 5 g/kWh to 10 g/kWh lower on methanol. The combustion temperatures on methanol were low compared to on gasoline. These occured when comparing the mean temperature of the exhaust gases, which were 2%–7% lower on methanol relative to gasoline. With a 1.8 l four-cylinder engine, the results showed that elevated levels of internal EGR might cause the strong influence of engine speed on the amount of NO_x emissions at 20 Nm at low rpm. At low load, the vacuum in the intake due to throttling is quite considerable (Verhelst et al. 2010). However, at 80 Nm the internal EGR levels are much

lower, which explained the higher NO_x emissions for gasoline and methanol at 80 Nm load level.

Liao et al. (2006) investigated the effects of the addition of methanol on pollution emissions. The experimental measurement was conducted in terms of HC, CO, and NO_x emissions at 358 K and the reference point was the gasoline-air mixture ($\varphi = 1.0$). The results showed that the addition of methanol has led to a major increment of HC emissions through fuel evaporation for rich fuel mixtures. The researchers also noted the relatively lean mixture which can be supplied to realise the rapid combustion for mixed fuel, compared to unleaded gasoline. They suggested comparing the emission characteristics at their separated optimisation equivalence ratio, to further explore the effect of methanol addition on the emissions.

The above results were similar to those of Canakci et al. (2013), Costa and Sodré (2010), Abdel-Rahman and Osman (1997), and Stein, House, and Leone (2009) who found that the volume of ethanol in gasoline affects the performance and emissions of the engine but results depend on the operating conditions. Previous researches have noted that NO_x emission can either decrease or increase depending on the engine operating condition rather than the higher ethanol blends (Chala, Aziz, and Hagos 2017; Karavalakis et al. 2012; Karavalakis, Short, Russell, et al. 2014; Karavalakis, Short, Vu, et al. 2014; Myung et al. 2012).

3.2.4. HC emission
3.2.4.1. Effect of ethanol-gasoline blends on HC emission.
Saikrishnan, Karthikeyan, and Jayaprabakar (2018) investigated the effect of ethanol-gasoline blends as fuel on performance and exhaust emission using a 3-cylinder, 4-stroke SI engine with varying torque conditions and constant engine speed of 5500 rpm. The results depict that the HC emissions decrease compared to pure gasoline fuel at different blends (E0, E5, E10, and E15). This can be attributed to the decrease in the stoichiometric air–fuel ratio of the ethanol fuel blends and increased in the actual air–fuel ratio of the ethanol blends due to the oxygen content.

Another similar work by Karthikeyan, Venkatesh, and Ramkumar (2017) found that HC emissions for bioethanol blends are lower than those for gasoline fuel at a constant speed of 2500 rpm. The HC emission for B20 (bioethanol blend) was nearly 20% lower than gasoline. The existence of oxygen in the fuel promotes complete combustion that leads to lowering of HC emissions. Similar results were obtained by many researches (Hsieh et al. 2002; Topgül et al. 2006; Yücesu et al. 2006, 2007). Additionally, the higher the compression ratio the higher is the surface to volume ratio caused by the higher HC emissions (Yang et al. 1993).

Doğan et al. (2017) studied the effects of ethanol-gasoline blends used in a four-cylinder, four-stroke SI engine for performance and emission analysis under full load. In this experiment, HC emissions were measured to be higher for tested ethanol containing fuels. The results indicate that HC emissions decrease with an increase in engine speed for all blend fuels. This is due to the more homogenous mixture which is obtained inside the cylinder with increased engine speed; HC emission shows a decreasing tendency. Findings were that with the decreased temperature inside the cylinder when ethanol ratio is added, the HC emission goes high. Therefore, the lowest HC emission was

observed at 4000 rpm with E0 and the highest at 2000 rpm with E30, and in the formation of HC emission, heat is very important as well as time.

Lin, Chang, and Hsieh (2010) investigated the behaviour of ethanol-gasoline blends (E0, E3, E6, and E9) used as fuel in a small four-stroke engine generator under different loadings. In the engine tests, HC emissions drastically decreased for all the fuel blend at different loadings compared to E0 (gasoline). The experimental results showed that the significant increases were observed in HC emissions when running with E9 fuels compared to E3 and E6. Also, when E6 is used as fuel, the HC concentration is less than the other fuels for each engine loading. The concentration of HC emissions decreases with the increase of the relative air–fuel ratio; the reason for the decrease of HC concentration in most cases (according to literature) is similar to that of CO concentration (Feng et al. 2015; Koç et al. 2009; Singh, Dhar, and Agarwal 2015). This decrease also depends on the combustion process in SI engines which is highly influenced by the combined effect of various parameters (Çay et al. 2013; Hosoz et al. 2013; Wong et al. 2015).

3.2.4.2. Effect of methanol-gasoline blends on HC emission.
Wu et al. (2016) compared the idle lean burn characteristics of an engine fuelled with methanol and gasoline, and explored an effective way to improve the economy and emission performance of engines under idle condition. The experiments were conducted at an idle speed of 800 rpm and $\lambda = 1.0$, $\lambda = 1.2$, and $\lambda = 1.4$, respectively. It was observed that HC emissions for methanol and gasoline were decreased at excess air coefficients of ($\lambda = 1.0$ to $\lambda = 1.2$) and then increased from $\lambda = 1.2$ to $\lambda = 1.4$. This is due to appropriable lean burn condition at ($\lambda = 1.2$) which benefits the complete combustion. Moreover, with further dilution of the air–fuel mixture ($\lambda = 1.4$), the instability of combustion would be amplified, which leads to more HC emission.

Alexandru, Ilie, and Dragos (2017) compared the effects of methanol-gasoline blends (M5, M10, M15, M20, and M25) on engine performance, combustion and emission characteristics in a single cylinder SI engine at two different engine speeds (3600 rpm and 4600 rpm). The results indicate a variation of HC emissions, which can rise rapidly with respect to a high number of load due to incomplete combustion or heat losses in the cylinder. The increase of the HC emissions can also be caused by the existence of regional lean and rich mixtures in the combustion chamber. Lean burn is considered as an effective means to improve thermal efficiency and reduce emissions of engines (Lee and Reitz 2003; Park et al. 2012; Wang et al. 2012). However, its application in engines fuelled with gasoline is limited due to the narrow, lean burn limit and slower flame speed of gasoline (Ji and Wang 2010) (Tables 3 and 4).

4. Conclusions

Ethanol and methanol are both promising and representative alternative fuels for SI engines. Ethanol and methanol fuels can be used as substitutes for gasoline fuels in SI engines without any further modification. The literature review shows that the emissions for methanol-gasoline and ethanol-gasoline blends are lower than that of pure gasoline fuel. The engine performance and exhaust emissions of ethanol-gasoline blends fuels are slightly different from methanol-gasoline blends; this is due to the influence of the combustion-related properties and operating conditions. However, some of the key findings of this review are summarised below.

1. For ethanol-gasoline blends, NO_x emission can either decrease or increase as reported by various researchers. These inconsistencies occur due to many factors. Firstly, when the combustion process is closer to stoichiometric, the flame temperature increases, therefore, the NO_x emission increases. Secondly, forced induction increases the fraction of NO_x, especially at high engine load with increases in CR. Therefore, when the injection ratio decreases due to an increase in the cooling effect of blends, the cylinder gas pressure and the thermal efficiency are slightly decrease which leads to a decrease in NO_x. However, for methanol blends, most of the NO_x emissions decrease in relation to CR and engine speed.
2. In most of the cases, BTE is higher when a methanol-gasoline blend is used. The maximum BTE is observed at 30% for M30 when the engine load is high and 6.8% with an increase in blend ratio and engine speed. These emission trends differ from the ethanol-gasoline blend, where BTE increases with an increase in ethanol blend, and decreases when the engine speed increases.
3. Methanol blends show a significant reduction in CO compared to ethanol blends. The maximum reduction value of CO is 55.5% for M10 as fuel at CR 7:1, and for ethanol, the maximum reduction of CO is 35% for E10 at CR 6:1.
4. The literature reported in this study shows that at low engine load and different operating conditions, an ethanol-gasoline blend results in complete combustion and subsequently reduces the HC and CO_2 compared to a methanol-gasoline blend.
5. As the CR increases, the engine torque and power increases with an increase in methanol or ethanol blend ratio, and brake power increases with an increase in BSFC for methanol blends. According to the reviewed articles, methanol has a negative effect on the BSFC and some of the results shows decreases in BSFC. Ethanol-gasoline has attained more benefits compared to methanol-gasoline in terms of exhaust emissions, engine power, and torque output, especially at low engine speed.

In conclusion, not all ethanol and methanol blends bring benefit to the environment concerning emissions and performance. Assessment needs to be made for each type of raw material, location and the method of extraction. This study shows that the significance of adding ethanol or methanol to gasoline are reduced engine-out emissions and increased efficiency, and that the impact changes with the blend ratio. The use of ethanol-gasoline blend fuels increase the brake power and torque output and decreases the BSFC. Methanol-gasoline blend fuels show slight increment in brake power and torque output, and higher BSFC than gasoline. Also, a larger content of gasoline fuel with a small ratio of ethanol injected into the cylinder increases brake power and torque output due to the higher density of ethanol.

Table 3. The effect of ethanol blends on engine performance and emissions (A review of the most recent experiments from 2018 to 2013).

Reference	Engine type	Blending ratio	Operating conditions	Engine performance				Emissions			
				BFSC	BTE	BP	T	CO_2	CO	HC	NO_x
1. Wang et al. (2018)	TC DISI, 3.5:1 CR	E10, E20, E30, E40, E50 + E 60	Operated at knock-free load conditions, constant speed	–	↓ by 7.07%	–	–	↑ by 21.2% E10 + E30	–	–	–
2. Saikrishnan, Karthikeyan, and Jayaprabakar (2018)	Single cylinder, 4-stroke SI engine, 88 mm bore, 64 mm stroke, 8:1 CR	E10, E20, E30 + E40	8:1 CR, 1250–3750 rpm, Max. Power (KW/rpm) 9.6/3500, Max. Torque (Nm/rpm) 26.48/2500, Air-cooled	E10, BSFC↑ E30, BSFC↓	–	E10, BF↓ E40, BF↑	E10 + E40, T↑ E30, T↓	E10, CO_2↓ E40, CO_2↑	E10, CO↑ E30, CO↓	E10, HC↑ E40, HC↓	–
3. Tekin and Saridemir (2017)	64 mm stroke, 8:1 CR, 4-stroke SI engine, 64 mm bore, 45 mm stroke, 163.46 cc capacity, 196cc displacement	E10, E20, E30 E40, E40 + E50	1500–3500 rpm, Max. horsepower (HP/rpm) 6.5/3600, Max. Torque (Nm/rpm) 13/2500, Air-cooled	E10,E20,E60, BSFC↑ E20, E30, BSFC↓	E20, E30, BTE↑[a] At Max. N, BTE↓	N↑, BP↑	E20, T↑[a]	E↑, CO_2↑ N↓	E↑, CO↓, N↑, CO↑	E↑, HC↓	–
4. Nwufo et al. (2017)	3-cylinder, 4-stroke SI engine, 68.5 mm bore, 72 mm stroke, 25cc Fuel consumption	E0, E5, E10 + E15	Varying engine torque, constant speed 2000 rpm, speed rate 5500 rpm, Power rate 29.5 KW, Water-cooled	T↑, BSFC↓	T↑, BTE↑	BP↑	–	CO_2↑ at all blends	E↑, CO↓	E↑, HC↓	NOx↓
5. Doğan et al. (2017)	4-cylinder, 4-stroke SI engine, 73.96 mm bore, 75.48 mm Stroke, 1297 cc cylinder vol	E0, E10, E20 + E30	8.8:1 CR, 2000–4500 rpm, Max. Power 43KW/5000 rpm, Max. Torque 98Nm /2500 rpm, 1-2-4-3 order, Idle speed 750 rpm, 12°BTDC-48°ABDC, 13–16 bar CP	E0, BSFC↓ 3000 rpm E30, BSFC↑ (Max. N)	N↑, BTE↓	N↑, BP↑	E0, Max. T↑[a] E30, T↓ (Max. N)	E0, CO_2↑ 300 rpm	E0, CO↑ E30, CO↓	N↑, HC↓	E30, NOx↓
6. Li et al. (2017)	Single cylinder, 4-valves PFI-SI engine, 90.3 mm bore, 90.1 mm stroke, 575 cm³ displaced vol., 150.7 mm connecting rod length	E0 + E30	9.6:1 CR, constant speed 1200 rpm, 3–5 bar (BMEP), under WOT, constant ignition timing, under stoichiometric conditions	E↑, BSFC↑ BMEP↓, BSFC↑	E0, BTE↑ 21.56% BTE↑ at all blends BMEP↑, BTE↑	–	–	–	CO↑ at all blends	HC↓	NOx↓ BMEP, NOx↑ 5bar
7. Karthikeyan, Venkatesh, and Ramkumar (2017)	3-cylinder, 4-stroke SI Engine, 68.5 mm bore, 72 mm stroke	E10 + E20	8.1:1 CR, constant speed 2500 rpm, Power KW/rpm	E↑, BSFC↑ low load	E↑, BTE↑ high load	–	–	CO_2↓ at all blends	CO↓	E20, HC↓ 20%	NOx↓
8. Ojapah, Zhao, and Zhang (2016)	Single cylinder, 4-stroke DISI engine, 81.6 mm bore, 66.94 mm stroke	E0, E15 + E85	11.78:1 CR, engine speed 0–6500 rpm, 3.2 bar IMEP, load conditions, 20 °C intake temp., stoichiometric conditions	E15, BSFC↓ at PVO E85, BSFC↑ at TSIO	E0, BTE↓ at EIVC E85, BTE↑ at PVO	–	–	–	E15, CO↓ at CAI E85, CO↑ at EIVC	E15, HC↓ at CAI E85, HC↑ at EIVC	–
9. Thangavel et al. (2016)	Single cylinder, 4-stroke SI engine, 200cc capacity	E30 + E50	9.4:1 CR, constant speed 3000 rpm, Power KW/rpm, 6.5/5000, 5-7-8.9 bar load IMEP, at 4 different throttles. Air-cooled, Stoichiometric condition Φ = 1 ± 0.03	–	E30, BTE↑	–	E30, T↑	–	E50, CO↑	↑, HC↓	E50, NOx↑

Table 3. Continued.

Reference	Engine type	Blending ratio	Operating conditions	Engine performance				Emissions			
				BFSC	BTE	BP	T	CO_2	CO	HC	NO_x
10. Iodice et al. (2016)	Euro-3, 4-stroke SI engine, 998 cm³ displacement, 189 kg Weight	E0, E10, E20 + E30	Max. Power 105.2 KW/10000 rpm, 20 °C constant temp., at cold start conditions	–	–	–	–	–	E20, CO↓ + E30, CO↑	HC↓ at CEE + HC↑ at CEE	–
11. Wang, Chen et al. (2015)	4 cylinder, PFI-SI engine, 75 mm bore, 84.4 mm stroke, 1.5L displacement	E0, E10 + E10W	10.5:1, constant speed 2000 rpm, at various loads	–	–	–	–	E10, CO_2↓	CO↓ at 10Nm	HC↓	NOx↑ when load ↑
12. Abdullah et al. (2015)	Single cylinder, 4-stroke SI Engine, 68 mm bore, 45 mm Stroke, 163 cm³ displaced	E0, E10, E20 + E30	9.0:1 CR, 2500–3000 rpm, 2 Nm-constant load, air-cooled, net power HP/rpm, 4.8/3600, net torque, Nm/rpm 10.3/2500	E20, BSFC↓	–	–	–	E20, CO_2↑ high % N↑, CO_2↑	E↑, CO↓	–	N↑, NOx↓
13. Elfasakhany (2014)	Single cylinder, 4-stroke with carburettor SI engine, 65.4 mm bore, 44.4 mm stroke, 0.6 L17 kg weight, 79.55 mm Connecting rod	E0, E3, E7 + E10	7:1 CR, varying engine speed 2600–3500 rpm, Power 1.5 KW at WOT condition, air-cooled	E10, BSFC↓ 2800 rpm	–	E10, BP↑ 3000 rpm	E0, T↑ lowest E10, T↑ 3000 rpm	CO_2↑	CO↓ at all blends	E↑, HC↓	–
14. Türköz et al. (2014)	4-cylinder, 4-stroke SI engine, 1581 cm³ displacement, max. power 185KW/7000 rpm, 1.61 carburettor	E85	9.2:1 CR, 2000–4000 rpm, constant throttle position, under stoichiometric fuel/air ratio, at WOT condition, under various ignition timing, water-cooled	–	–	BP↑ at 6°–4° adv. IT	T↑ at 4° 4000 rpm	CO_2↓	CO↑	HC↓ at −2°	NOx↑ IT↑
15. Ghazikhani et al. (2013)	Single cylinder, 2-stroke SI engine, 35 mm bore, 35 mm stroke, 34 mL displacement, 1 cc consumption	E5, E10 + E15	6:1 CR, 2500–4500 rpm, at various engine velocities + load, nominal power output KW/rpm 0.5/4000, water-cooled	BFSC↓ at all blends	–	–	–	CO_2↓ with 6.3%	CO↓ with 35%	HC↓	NOx↓

Notes: [a] = at engine speed 2500 rpm; + = and; ↑ = increase; ↓ = decrease; N = engine speed; N↑ = when engine speed increase; N↓ = when engine speed decrease; CR = compression ratio; CP = compressive pressure; PFI = port fuel ignition; SI = spark ignition; CEE = cold extra emission; CAI = controlled auto-ignition; EIVC = early intake-valve closing; PVO = positive valve overlap; TSIO = throttled spark ignition operations; Adv. IT = advanced ignition timing; DISI = direct injection spark ignition; WOT = wide open throttle; Max. = Maximum.

Table 4. The effect of methanol blends on engine performance and emissions (A review of the most recent experiments from 2018 to 2013).

Reference	Engine type	Blending ratio	Operating conditions	Engine performance				Emissions			
				BFSC	BTE	BP	T	CO_2	CO	HC	NO_x
1. Wani (2018)	Single cylinder, 4-stroke SI engine, 500 cc displaced, speed rate 6000 rpm	M0, M15, M30, M45, M60 + M75	9:1 CR, 0–8000 rpm, at stoichiometric air/fuel ratio, at high octane rate	BSFC↑ at all blends	–	M, BP↓ at all blends M0, BP↑	T↑ at 2000 rpm	–	CO↑ at all blends	HC↑	NO_x↓
2. Alexandru, Ilie, and Dragos (2017)	Single cylinder, 4-stroke SI engine, 72 mm bore, 60 mm stroke, 244 cc displacement	M5, M10, M15, M20 + M25	9.8:1 CR, 2000–7000 rpm, Max. Power 17HP/7000 rpm, at various loads, air-cooled	–	–	M, BP↑ N↑	M5, T↑ at 5000 rpm	M, CO_2↓[a]	M, CO↓[b]	M, HC↑[a]	–
3. Divakar Shetty and Antony (2017)	Single cylinder, 4-stroke SI engine, 70 mm bore, 66.7 mm stroke, 256 cc displacement	M10, M15, M20, M25 + M30	4.5–10.5:1 CR, varying load, 28°BTDC-32°BTDC, Power 2.8KW/3000 rpm, water-cooled	–	M30, BTE↑[a] 30%	M30, BP↑[a]	–	CO_2↑[a]	CO↓ at all blends	M↑, HC↓	NO_x↓
4. Sharudin et al. (2017)	4-cylinder, Multipoint port fuel system SI engine, 1.6 L displacement, 78 mm bore, 84 mm stroke, 159 capacity, 138 kg weight	M5	10:1 CR, 1000–2500 rpm, at constant throttle 100%	BSFC↑ at 1000 rpm	BTE↑ at 2500	BP↑ 3.9%	–	CO_2↑[c]	CO↓[c]	HC↓[c]	NO_x↓[c]
5. Yao, Ling, and Wu (2016)	4-cylinder, 4-stroke PFI SI engine, 78.7 mm bore, 69 mm stroke, 1.342 L displacement, 16 valves	M0, M10, M20, M30, M50 + M70	9.3:1 CR, 1200–2800 rpm, in-cylinder mixture air-fuel ration, Max. Power 63.2KW/, Max. Torque 109.8Nm/ 5200 rpm, water-cooled	–	–	–	–	–	CO↓	M50, M70, HC↓	NO_x↓
6. Elfasakhany (2015)	Single cylinder, 4-stroke SI engine, 65.1 mm bore, 44.4 mm stroke	M3, M7 + M10	7:1 CR, 2600–3450 rpm, 1.3–1.6 KW load, air-cooled	–	–	–	–	CO_2↑ at all blends	M10, CO↓ 55.5%	HC↓ at all blends	–
7. Danaiah, Kumar, and Kumar (2014)	4-cylinder, 4-stroke carburettor type gasoline engine, 73.02 mm bore, 88.9 mm stroke	M5, M10 + M15	10°–30° BTDC, variable load, water-cooled, rated power rated speed 1500 rpm	M5, BSFC↓ 10° + 20°, M10 + M15, BSFC↓ full load	BTE↑ at all blends M5, BTE↑ higher at 30°	–	–	–	CO↓	–	NO_x↓
8. Varol et al. (2014)	4-cylinder, 4-stroke, MPI- 89 mm bore, 95 mm stroke	M10	11.1:1 CR, 1000–4000 rpm opening pressure 5bar, rate power 55KW/3600 rpm	BSFC↓ N↑	BTE↑ N↑ 6.8%	–	–	CO_2↓ N↑	CO↓ N↑	HC↓ 13.4%	–
9. Ni et al. (2014)	Single cylinder, 4-stroke SI engine, 68 mm bore, 45 mm 163 cm³ displacement	M15 + M25	8.5:1 CR, 1800/3600 rpm, air-coooled, idling, rate power 3.5KW/3600 rpm	BSFC↓ at all loads	–	–	–	–	M25, CO↓ at all blends	M↑, HC↓	NO_x↑
10. Altun et al. (2013)	4 cylinder, 4-stroke SI engine, 89 mm bore, 95 mm stroke	M5 + M10	11.1:1 CR, 1000–4000 rpm at various throttle opening positions, water-cooled, opening pressure 5bar	BSFC↑	BTE↑	–	–	M5, CO_2↑	CO↓	HC↓ at all blends	–
11. Danaiah, Kumar, and Kumar (2013)	4 cylinder, 4-stroke SI engine, 73.02 mm bore, 88.9 mm stroke	M5, M10 + M15	At various engine load, rate power 17.5HP, rate speed 1500 rpm	BSFC↓ BSFC↓ at all blends	M15, BTE↑	BP↑ when BSFC↑	–	CO_2↓ at all blends	M15, CO↓ highest	HC↓	NO_x↓

Notes: [a] = at high engine load; [b] = at low engine load; [c] = at all engine speed; EFI = electronic fuel injection; MPPI = Multi-point port injection; + = and; ↑ = increase; ↓ = decrease; N = engine speed; N↑ = when engine speed increase; N↓ = when engine speed decrease; CR = compression ratio; PFI = port fuel ignition; SI = spark ignition.

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Chapter 4: Paper 3

Effect of cold start emissions from gasoline-fueled engines of light-duty vehicles at low and high ambient temperatures: Recent trends

This chapter surveys the recent trends in cold-start emission behavior regarding the impact of changes in ambient temperature in relation to the advanced technology of gasoline direct injection (GDI) and port fuel injection (PFI) vehicles. It also presents the influence of lower combustion temperature and rich air/fuel mixture at very low temperature conditions. The article has been published in the *Case Studies in Thermal Engineering*, ELSEVIER BV.

Effect of cold start emissions from gasoline-fueled engines of light-duty vehicles at low and high ambient temperatures: Recent trends

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A R T I C L E   I N F O

A B S T R A C T

The cold-start condition is an important factor affecting vehicle emissions from gasoline direct injection (GDI) and port fuel injection (PFI) vehicles. This paper studied the recent trends in cold-start emissive behavior with the impact of changes in ambient temperature over the advance technology GDI and PFI vehicles. This research surveys the approaches taken to reduce engine-out emissions and tailpipe emission challenges during cold-start and transient operation using technological advancement. It was found that ambient temperature had a significant influence on cold start emissions especially when the combustion temperature was lower, and when the air/fuel mixture was very rich at very low temperature conditions. Some vehicular emissions increased by 10 times as the temperature varied from $+30\ °C$ to $-7\ °C$ and fuel consumption increased as well. GDI vehicles exhibit lower fuel consumption than PFI vehicles but emit more PM mass and solid PN. These results indicate that the particulate emissions from PFI vehicles should not be neglected compared to those from GDI vehicles, especially in a cold environment.

1. Introduction

Transport activities contribute significantly towards air-polluting vehicle emissions in the world. In order to improve air quality and quantify the environmental impact caused by road transport, analytical and experimental studies are essential for policy makers and researchers [1]. Several previous studies have suggested that engine-out emissions can be controlled using various modification techniques, namely, engine modification, fuel modification (ethanol-gasoline blends) and exhaust gas treatment (exhaust gas ignition and catalytic converters). Engine technology is one of the major factors affecting vehicle emissions. There are two main types of fuel injection technology for gasoline-fueled vehicles namely, GDI and PFI [2]. Generally, GDI provides effective fuel economy and lower greenhouse gas emissions, because direct fuel injection technology can more accurately control fuel volume and injection timing [3,4]. PFI is the prevalent technology in current production light-duty vehicles [5]. Ethanol-gasoline blends have several reported advantages which include increasing oxygen content and decreasing tailpipe emissions, according to various researchers [6–12]. Gasoline-fueled vehicles are liable to produce excessive emissions when started at low ambient temperatures [13]. For new vehicles, little data are available to show the influence of gasoline-ethanol blends on exhaust emissions, especially related to the cold and warm start processes, therefore investigation of the relevant cold emission factors was considered necessary. Both cold and warm starts are classified as transient processes of an internal combustion (IC) engine [14].

Catalytic converters are not designed to have any specific influence on combustion of particulate matter (PM) from gasoline-fueled engines; they are designed to clear the incomplete combustion process performed by the engine and to lead the exhaust gas

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mixture to equilibrium composition at relatively low temperatures [15]. This device contains a catalyst for converting carbon monoxide (CO), hydrocarbons (HCs), and nitrogen oxides (NOx) in the exhaust system into less harmful ones such as carbon dioxide (CO_2) and water (H_2O) [16,17]. This paper studied the recent trends in modern technology PFI and GDI vehicles cold-start emissive behavior in relation to changes in the ambient temperature. In this context, the approaches taken to reduce engine-out emissions and tailpipe emissions thus far during cold-start and transient operation using modern technology PFI and GDI vehicles are discussed.

2. Effect of cold-start and ambient temperature conditions

The cold-start condition is an important factor affecting vehicle emissions from GDI and PFI engines. The release of noxious or toxic substances into the air from light-duty gasoline vehicles are an important source of urban air pollution [18,19]. To regulate these substances, vehicles have been required to meet strict emissions standards for PM, NOx, CO, and HC over the last several decades [20]. This has pushed the industry and researchers to upgrade engine calibration, engine design, and after-treatment technologies.

2.1. Effect of cold start conditions on PM emissions

There are ongoing researches on PM emissions from GDI vehicles, but very few have evaluated PFI vehicles, because PFI vehicles generate low volumes of PM emissions into the environment. Particulate studies for GDI vehicles are essential, and particulate emissions from PFI vehicles should attract manufacturers', researchers' and policy makers' attention. Previous research shows that GDI engines have higher PM mass [21–24] higher particle number [25,26] and higher emissions than PFI engines. Various studies have investigated how to improve GDI engine designs and calibrations to decrease PM emissions using different fuel-injection strategies to influence PM emissions [27–29].

During cold start, particle number emissions are significantly higher than after the engine has warmed up to its normal operating temperature [30]. Different researches have been conducted on the effect of cold start [1,31–37] but few quantify the particle number distributions during cold start gas-phase emissions [14,38–40]. In a recent study [38], quantified the primary particle size distributions for PFI and GDI vehicles. It was found that 377 and 307 particles were calculated from the TEM images for the GDI and PFI vehicle emissions, respectively (Fig. 1a and b). It was noticed that acceleration had an influence on the PM emissions under warm start conditions, while the torque variation had a clear impact on the PFI vehicle PM emissions under cold start conditions. The particles emitted from the GDI vehicle are of an ordered nanostructure with higher crystalline height, length and longer fringe length (TEM image of GDI emissions, 10 nm scale), compared to the morphological structure of PFI emissions, which decreases the feasibility of further oxidization [22,41,42]. Robinson et al. [39] measured the different particle sizes emitted during each phase for different lengths of time. Fig. 2 shows the different phases of engine exhaust particle size (EEPS) and number distributions through the period of cold start with respect to engine speed and exhaust temperature. At the end of the cold start phase (237 s), the smallest particles measured by the EEPS (5.6 nm to ~10 nm) were no longer detectable due to very low concentrations (from 237 s to 330 s). This indicated that the catalyst was efficiently removing compounds that could potentially nucleate to particles [43,44]. When RPM increased, which again indicates acceleration, 6 nm to ~154 nm particle size concentrations increased with the highest concentrations being of size 10 nm and 30 nm. However, the highest particle number concentrations occurred for particles in the nano-particle (Dp < 50 nm) range, which accounted for over 97% of the particles for the entire cold start (Phases 1 to 3). These trends are similar to those found by Refs. [45,46].

Price et al. [40] quantified the cold start size distribution and composition of particle number emissions from a direct injection gasoline engine. As indicated (Fig. 3), the particles were collected at an axial distance of 137 mm from the plane where the aerosol enters the classifier column. The individual particle size was 10 nm–30 nm and the aggregate size was 30 nm–100 nm. The particle
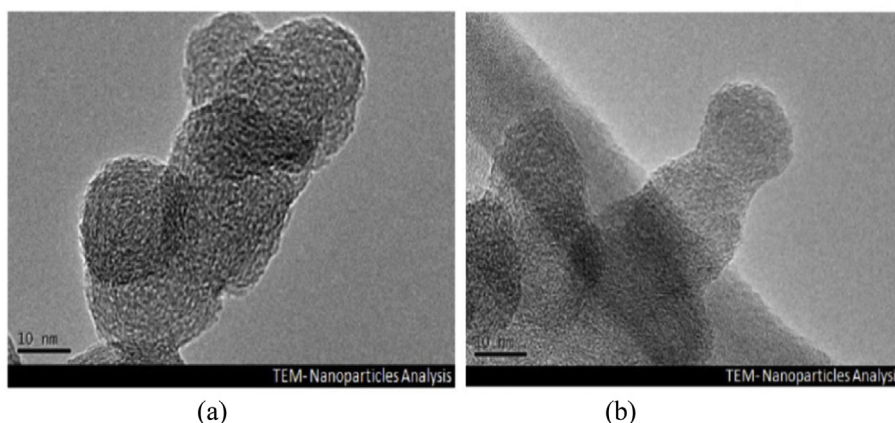

Fig. 1. The aggregate particles in the TEM images for 10 nm scale of (a) GDI vehicle and (b) PFI vehicle [38].
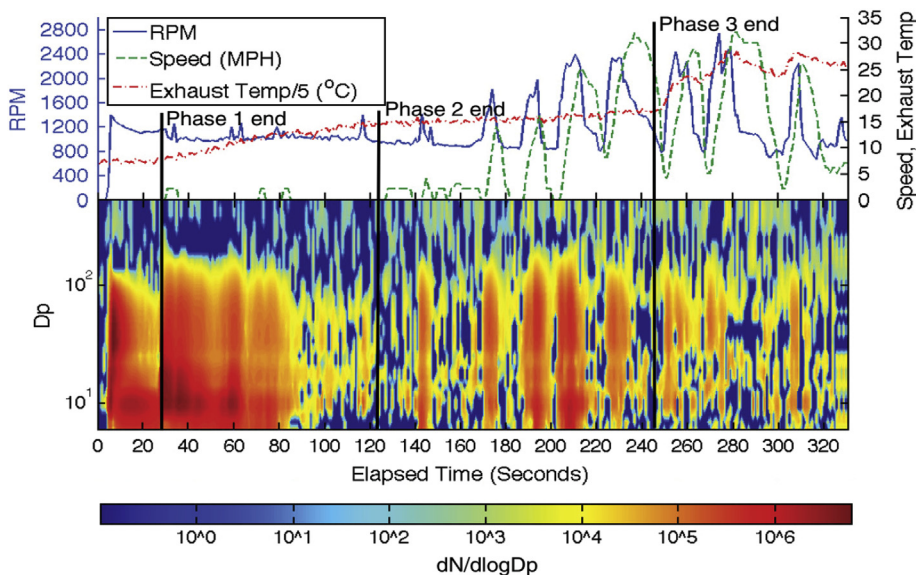
Fig. 2. Particle number distribution (bottom panel) over first 330 s, with time-aligned data on engine speed and exhaust temperature (upper panel) [39].
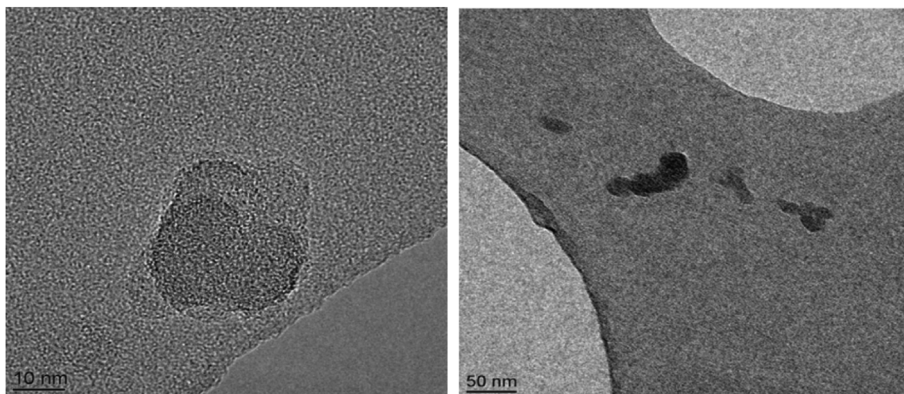

Fig. 3. HR-TEM images of combustion generated particles sampled at 10 nm and 50 nm on the modified DMS500 space charge guard [40].

size and particle number emissions were found to decrease over time during engine warm-up. It was concluded that only 29% of particles were in the solid phase, with elemental carbon being between 5 nm and 10 nm and carbonaceous particles in the 30 nm–80 nm range.

2.2. Effect of ambient temperature conditions on gasoline-fueled vehicles

Another significant factor that affects vehicle emissions is ambient temperature. Chan et al. [47] found that ambient temperature had a significant influence on cold start emissions, and some emissions increased by 10 times as the temperature varied from $+22\,°C$ to $-18\,°C$. Mamakos et al. [48] investigated the effect of ambient temperature on particulate emissions using different driving cycles. It was observed that the PM emissions increased by approximately 150%–200% with the New European Diving Cycle, but with the Common Artemis Driving Cycle were nearly constant when the temperature varied from $+22\,°C$ to $-7\,°C$. R. Zhu et al. [2] studied the effect of two-fuel injection technology and ambient temperature on fuel consumption, gaseous and particulate emissions. The results showed that a decrease in ambient temperature from $30\,°C$ to $-7\,°C$ significantly increased fuel consumption and vehicle emissions except for NO_X. The GDI vehicle exhibited lower fuel consumption than the PFI vehicle but emitted more PM mass and solid PN emissions at $30\,°C$. These results indicate that particulate emissions from a PFI vehicle should not be neglected compared to those from a GDI vehicle especially in a cold environment [24,49].

Iorio et al. [50] investigated the effect of octane rating of fuel by varying its ethanol blend content. It was found that the higher octane fuel had higher oxygenated fuel content, which led to lower PM emissions. Chan et al. [51] reported that E10 was found to reduce black carbon (BC) emissions from a GDI vehicle by 15% at standard temperature and by 75% at $19\,°F$ ($-7\,°C$). The use of
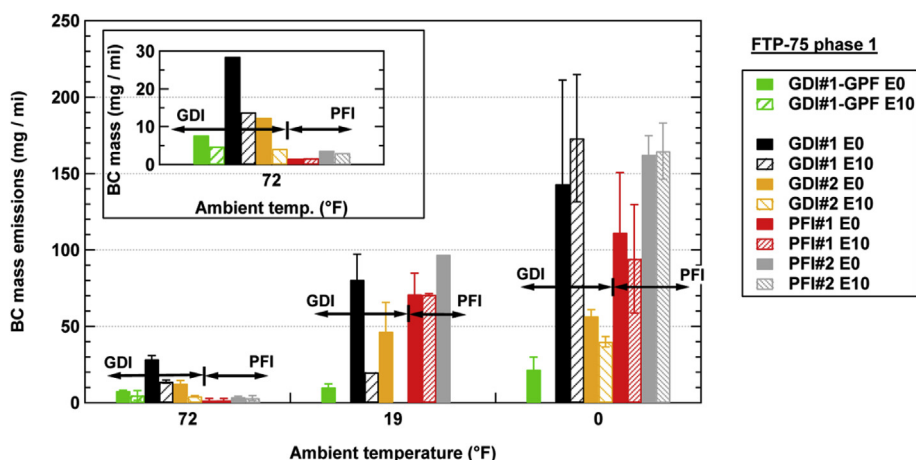
Fig. 4. BCE mass emissions from GDI and PFI vehicles at ambient temperature over the phase 1 portion of the FTP-75 drive cycle using E0 and E10 [51].

gasoline particulate filter (GPF) decreased BC emissions from the selected GDI vehicle by 73%–88% at various ambient temperatures over the U.S. Federal Testing Procedure 75 (FTP-75) phase 1 drive cycle. At ambient temperature, the particle emissions for a warmed-up engine had low impact. Fig. 4 compares the E0 with E0 ethanol blends results using GDI and PFI vehicles at ambient temperature over the phase 1 portion of the FTP-75 drive cycle under cold-start. It was observed that the PFI vehicle showed a lower BC mass of emissions when operated on E10 at 0 °F (−18 °C), but were not statistically different. It was suggested that E10 has some benefit for GDI engines [51].

Kunze et al. [52] reported that vehicle may produce good performance once fully warm, bad cold start performance may result in a vehicle failing key emission tests and being assigned a high fuel consumption rate. It is difficult to improve fuel consumption during the cold start and warm up phase [53], particularly as consumer driving habits often involve trips which are such a short distance that the engine never reaches its optimum operating temperature [52]. The appropriate increase in temperature of the lubricant during the warm-up phase results from the frictional dissipation in the engine systems such as the main bearings [53].

2.3. Effect of cold start and catalytic converter on CO, HC and NOx emissions

Among the various exhaust gas treatment processes, catalytic converters are the most commonly used in converting harmful CO, HC and NO_X emissions into CO_2, H_2O, O_2 and N_2 in stable engine running conditions [17]. The substrate used in a catalytic converter can be ceramic or metallic. Both substrate types have less significant effects on CO or NO_X conversion [54]. The catalysts must reach operating (light-off) temperatures above 204 °C–371 °C before significant pollutant conversion is achieved [55]. It has been suggested that the catalyst warm-up occurs more rapidly when the engine operates under heavier loads and when the catalyst is positioned closer to the engine [35]. Catalyst light-off is delayed at lower ambient temperatures and CO and HC are not oxidized in this system during the period immediately following start-up. These results are due to start-up events, which are significant in terms of emissions and fuel consumption, with a strong dependency on the temperatures of both the engine and ambient air [14]. Furthermore, start-up events are the most fundamental transient events experienced by automotive engines as the numerical values of engine speed and fuel consumption change from zero to non-zero values in a very short space of time, even before any power is transferred to the wheels [33]. The factors that affect emissions and fuel consumption during cold start at low ambient temperatures are summarized in Fig. 5.

Many studies on engine-out CO and HC emissions have been conducted for engines running at cold start conditions using catalytic converters. Raja & Arasu [54] investigated the effect of glow plug assisted exhaust gas ignition (EGI) and use of a catalytic converter on cold start emissions in a motorcycle engine fueled with ethanol-gasoline blends. The result shows that the cold start CO and HC emissions were less than that of pure gasoline (E0). At ambient temperature of 30 °C ± 1 °C, the highest emission reductions were observed with E10. This means that cold start emissions at normal ambient temperatures are several orders higher than those at warm start [47]. The HCs emitted in the cold part of the test increase at a high rate at lower ambient temperatures [14]. Iodice & Senatore [56] investigated the effects of ethanol-gasoline blends (G10, G20 and G30) on cold emissive behavior of a catalyst four-stroke motorcycle. The results showed that the ethanol added into gasoline decreased CO and HC cold start emissions. Among the blend fuels, G20 exhibited the greatest reduction (29% and 45% respectively) compared to pure gasoline (G0). High ethanol blend content results in less emission reduction than those of low ethanol blends (G10 and G20); this is due to the incomplete combustion that occurs in the combustion chamber during the transient time when the engine operates over a certain lean limit, and to the lower volatility of G30 blend fuel that decreases at higher ethanol content [1,37,57].

If the converter is heated to 600 K or above, the light-off time reduces to zero and both HC and CO emissions decrease significantly (Fig. 6). When the initial converter temperature varies from 300 K to 500 K, the tailpipe emissions remain nearly the same. Hence, for an active method to be effective, it must supply additional energy to raise the catalyst temperature beyond 600 K [58].

NO_X engine-out emissions are primarily influenced by three engine variables: the burned gas fraction in the in-cylinder unburned
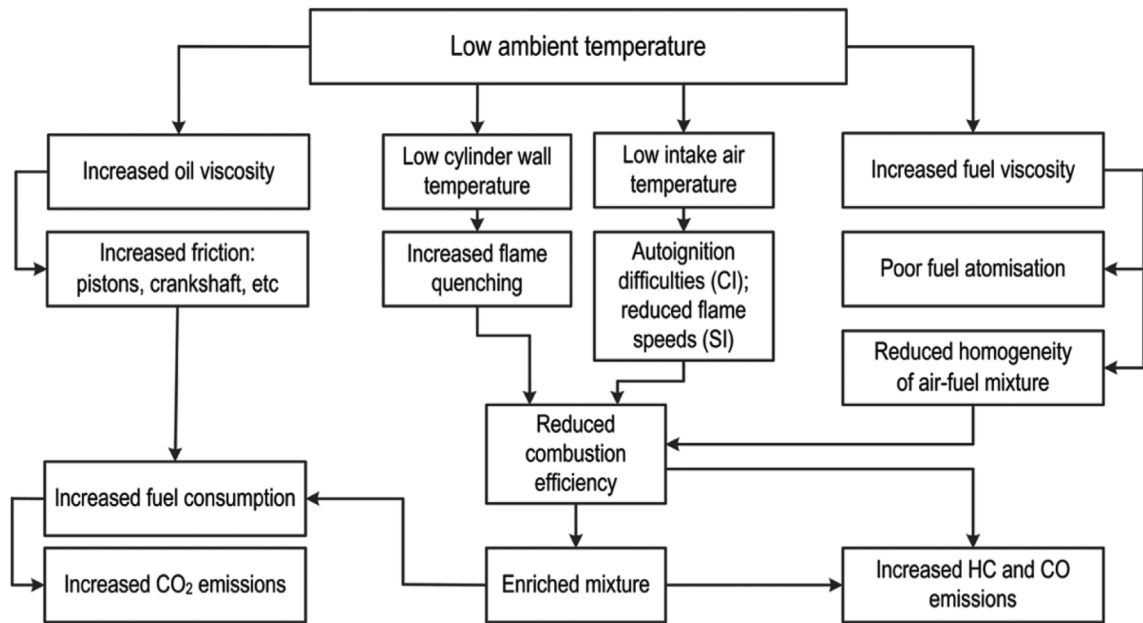
Fig. 5. Effect of cold start operation at low ambient temperatures on engine-out emissions [33].
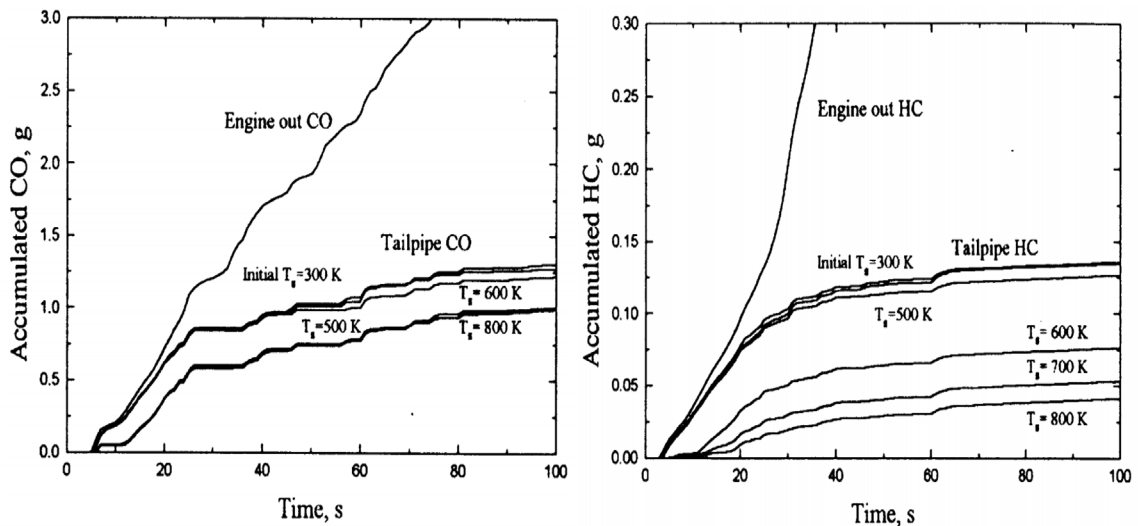

Fig. 6. Effect of different initial catalyst temperature on cold start CO and HC emissions during the first 100 s of the FTP-75 [58].

mixture (residual plus recycled exhaust gas), the air/fuel ratio, and the ignition timing [59]. As illustrated in Fig. 7, vehicle G3 showed a 30-fold increment of NO_X at −7 °C over the Urban Driving Cycle (UDC). During the first 50 s, the engine demonstrated high lambda values more than one (22 °C) because it was operating lean. This lean operation continued close to the end of the warming-up of the catalyst, indicated by the drop close to zero of the HC concentration [34]. The air/fuel mixture was rich until t ≈ 60 s to become lean immediately after until t ≈ 160 s (Fig. B). As reported by Ref. [60], a decrease in engine-out NO_X emissions is expected when the combustion temperature is lower, for example when the air/fuel mixture is very rich at very low temperature conditions and during cold-start.

As illustrated in Fig. 8, there are two peaks in the cycle for both NO_X and HC curve. The first peak of the NO and HC emission result is due to the exhaust valves opening or leakage in the cycle. For the second peak, the NO emissions decreased sharply, due to misfire occurrence. The second HC peak is due to some un-evaporated fuels impinging onto the piston top and liner in the first cycle and due to exhaust in the subsequent cycles. The unburned HC emissions decreased gradually in the subsequent cycles [61]. When the ignition timing was set to beat 5 °CA BTDC, the lowest NO emissions were generated in the cylinder and advance in the ignition timing caused an increase in the NO emissions, and an increase in in-cylinder temperature improved the in-cylinder mixture formation [61]. Table 1 shows some of the cold-start emissions at low and high ambient temperature using gasoline-fueled engines.
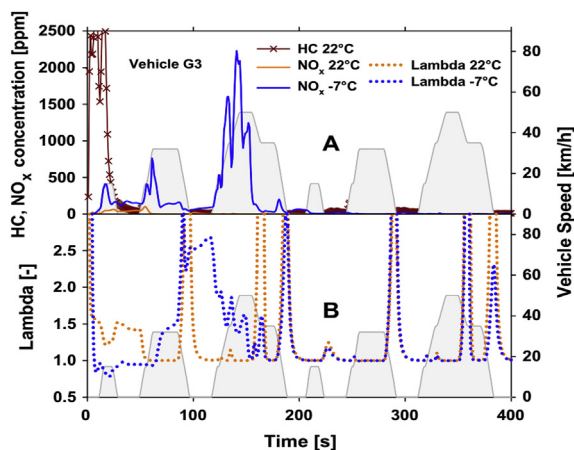
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Fig. 7. (A) NO$_X$ instantaneous emissions and (B) lambda value of vehicle G3 at both temperatures over the first half of the UDC [34].
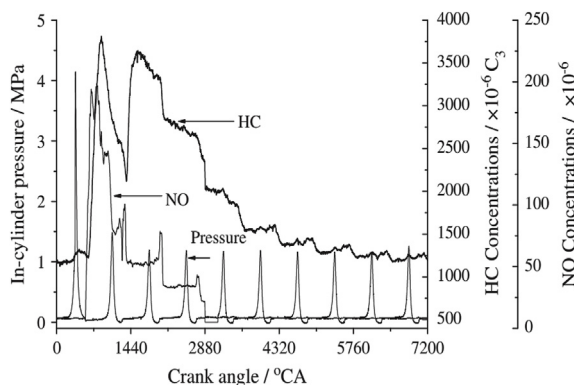

Fig. 8. Cold-start transient HC and NO emissions with fuel injection in the first cycle [61].

3. Different approaches for reducing vehicular emissions

Modification techniques using technological advancements can be used, but it is often uncertain how these affect emissions performance. To reduce tailpipe emissions and time for the catalytic converter to reach light-off temperature during cold-start, a combination of the following technologies and approaches may be taken, as outlined in the following studies. Khan, Zeeshan, & Iqbal [67] designed a non-noble metal-based catalytic converter for thermal management to decrease cold start emissions. They explored two different approaches: (1) use of phase change material (PCM) to keep the converter hot beyond light-off temperature during shorter soak times and (2) installation of glow plugs within the stainless steel pipe incorporated in the converter to heat it up before or after cold start and so avoid direct exposure of the catalyst at the higher temperatures of the glow plugs. Ando et al. [68] suggested that electrically heating up the converter before or after engine cold start-up can reduce cold start emissions. Relocating the catalytic converter closer to the engine is the most common approach used to reduce the time to light-off. This has proved an effective strategy in reducing emissions, but introduces unnecessary heat into the passenger compartment [30]. Another way to achieve similar result is to use a secondary air injection (SAI) system. This reduces HC emissions by 46%–88% and CO emissions by 37%–93% compared to operations without any secondary air during the first 25 s of the engine start-up process depending on the conditions [66].

In the previous research, honeycomb reactors have shown that catalytically active coating (washcoat) diffusion resistance has a significant effect on conversion of both steady state reactor operation and transient light-off [69,70]. Von Rickenbach et al. [71] modeled the heat transfer, finite rate washcoat diffusion and surface chemistry and boundary conditions in foam based catalytic reactors. This allowed them to identify the optimal foam parameters that lead to fast light-off for given operating conditions. The result showed that foam-based catalytic reactors have significant cold start emissions reduction compared to honeycomb reactors. Dudák et al. [72], explored a wide range of zeolite and alumina dual-layer configurations. They observed a higher CO conversion when the zeolite was coated as a top layer due to the higher macroporosity and low thickness of the coating. Alumina used as the top layer showed a significant effect on the catalyst performance, because alumina has a combination of Lewis acidity and basicity, has good porosity and high surface area [73]. Another way to achieve similar results is to use low aromatic fuels. A number of studies preformed on gasoline-fueled vehicles have shown decreases in tailpipe NOx emissions with decreases [5,74–76] and increases [77,78] in the aromatic content. These show that significant reduction in NO$_X$ emissions can be achieved when the aromatic

Table 1
Some of the effects of cold-start emissions from light-duty vehicles under low and high ambient temperature.

Type of vehicle	Fuel	Test conditions	Effects	Remarks	References
GDI-MPI 4-cylinder, 64 kPa/6000 rpm power, 1398 cm³ displacement	CUG with 95 RON, vapor pressure (at 37.8 °C) 67.3 kPa, 736.1 kg/m³ density	TWC + EGR, DF = V65 to 765, SSC, WLTC cold and warm	CO is negligible using GPF, HC↓, PN↓	GPF offers excellent potentials of emission reduction compared to TWC	[62]
GDI and PFI	CUG	World harmonized Light-duty Test Cycle (WLTC) at −7 °C and 23 °C, ambient conditions, RH: 50%	THC, CO, NOx, CO2 and N2O↑ at −7 °C for GDI and PFI	These pollutants are important sources of the most problematic pollutants in terms of harm to human health: PM, ground-level O₃ and NO₂	[63]
GDI vehicle: 4-cylinder, 1.8 L displacement, 9.6:1 CR; PFI vehicle: 4-cinder, 2.0L displacement, 9.8:1 CR, TWC	Ethanol fuel blend E10 with 82.37% C, 13.78% H, 3.85% O	Ambient temperature from 30 °C to −7 °C, China IV emissions test standards, WLTC version 5.3, CVS flow rates were set to 12 m³/min for gasoline tests and 18 m³/min for E10 tests, atmospheric pressure and relative humidity 101 kPa ± 1 kPa and 45 kPa ± 1%, respectively	Low FC in GDI (13%–14% at 30 °C and 17%–18% at −7 °C) than PFI; PM ↓b for GDI and PFI significantly ↑; THC↑ at 30 °C and ↓ at −7 °C for PFI; CO↓ for GDI	The FC of the PFI vehicle was more likely to be influenced by the LAT compared to the GDI vehicle, especially in the cold-start tests	[2]
MC: 4-stroke engines, and for pollutants abatement; TWC converters; Euro-3 legislative category and displacement [750 cm³]; 132 kW/12,500 rpm power; 13:1 CR	CUG with 95 RON, oxygenated additive (8.1 v/v %), 85.56 wt % C, 1.8 wt% O, 0.67 vol% benzene and 33.3 vol% ArC.	Tested under transient and steady-state (DCs): (ECE + EUDC), 20 km/h to 120 km/h at constant speed, 20 °C–25 °C at constant temp. for 8 h	CO and HC ↑a compared to warm engine	When the rich value of the air/fuel mixture and the catalytic converter fails to reach the light-off temperature, then the motorcycle will produce higher cold-start emissions of CO and unburned hydrocarbons	[64]
4-cylinder, 4-stroke, turbo-charged and inter-cooled 1.6 l, GDI engine; 10.5:1 CR; 130 kW/6000 rpm power	Unleaded gasoline with 96.5 RON, 31.8 vol% ArC, 86.01 wt % C, 0.9 wt% O, 13.09 wt% H, 57.8 kPa RVP	Operated under cold-start conditions for 15 min, 20 °C oil temp prior to engine start-up.	PN↓ by 65% at cold start test and PN density ↓ by 95%	i. The Influence of engine-out PM is more significant than the tailpipe-out PM during cold-start engine operation. ii. When the DR pre-TWC increases, the PN density increases due to nucleation of the volatile particles precursors present in the exhaust gas	[15]
1.8 L 4-cylinder heated injector vehicle test; 500 cm³ cylinder; 4 g/s at 420 kPa ISF	FTP-75 test at 20 °C with E22 and E100 fuel; 420 kPa fuel pressure; 7.5% RFVF	Operated under cold-start, FTP-75 test, −5 °C ambient temp. Multec® 3.5HT fuel injector	For E20: THC↓ 30%, CO↓ 22%, NOx↓ 2%, NMHC↓ 35%; For E100: THC↓ 66%, CO↓ 61%, NOx↓ 2%, NMHC↓ 69%	The Delphi heated injector system requires minimal engine hardware modifications and has been validated. This shows a significant reduction in emissions for Brazilian E100.	[65]
PFI-SI engine (GM 2.2L L61 Ecotec engine) with ECM, consist of cast-iron manifold, TWC converter and a muffler at the ES	Unleaded test gasoline (Indolene)	Tested under steady state cold-fluid, operated with various spark timings at a fixed condition of 1200 rpm, λ engine = 0.9, and 8.0 g/s intake air flow, 20 °C test-cell ambient conditions	HC ↓ by 46%–88%, and CO ↓ by 37%–93% using SAI system	Significant emissions reduction was achieved by the TOP prior to the catalyst. This enhances the chemical process occurring inside the catalyst through faster catalyst light-off	[66]

Note: Exhaust system (ES), Engine control module (ECM), Port-fuel injected (PFI), Spark-ignition (SI), Motorcycle (MC), Three-way catalyst (TWC), Commercial unleaded gasoline (CUG), Driving cycles-(DCs), ↑a at cold-start, ↑ increase, Research octane number (RON), Aromatic contents (ArC), Compression ratio (CR), Secondary air injection (SAI), Gasoline direct-injection (GDI), Reid vapor pressure (RVP), C-carbon, O-oxygen, H-hydrogen, DR-dilution ratio, Engine-out emission (pre-TWC), Required fuel vapor friction (RFVF), Extra-urban driving cycle (ECE + EUDC), Required fuel vapor friction (RFVF), FC-fuel consumption, ↓b When the ambient temperature decreased from 30 °C to −7 °C, Low ambient temperature (LAT), Non-methane hydrocarbons (NMHC), Relative humidity (RH), Steady state cycle (SSC), Nitrogen dioxide (NO₂), Thermal oxidation process (TOP).

component of fuel is low.

One promising idea is the use of advanced vehicle technologies being developed and implemented to meet both engine-out emissions and tailpipe emissions. One of these changes is from traditional three-way catalysts (TWCs) to catalyzed GPFs. GPFs are being developed for catalyzed applications in both the close-coupled and under-floor positions, where they combine the functionality of filtration and TWC [79]. Craig et al. [80], measured GDI vehicle emissions over the FTP-75 test cycle with a catalyzed GPF in the under-floor position. The result of the coated GPF showed that the tailpipe emissions of CO, THC and NOx were decreased by 86%, 38% and 34% respectively. There was a specific decrease in NO_X under the aggressive driving conditions of the US06 test cycle, leading to 88% decrease in NO_X compared to the baseline. These results are similar to those obtained by Refs. [62,81–83].

4. Conclusion

1. Inactivity of a vehicle for a long period and low ambient temperatures may increase the heating required for the catalytic converter to reach effective operating temperature, and may prolong the period of high exhaust emission rates.
2. It was observed that the change in fuel properties (such as aromatic content) affects particle formation during combustion as well as the cold and hot condition driveability of the vehicle. Further, the particle emissions form a gasoline-ethanol blend depends on the type of fuel injection system and the operating conditions of the vehicle.
3. The TWC was found to be active only after 120 s in converting cold-start emissions (CO, HC and NOx). TWC proves to be a better option than EGI in controlling cold start emissions with CUG or ethanol blends. Recent advances in vehicle technologies aim to meet both engine-out emissions and tailpipe emissions. One of these advances is to change traditional TWCs for catalyzed GPFs. GPFs are being developed for catalyzed applications in both close-coupled and under-floor positions, where they combine the functionality of filtration and TWC.
4. Advanced technologies have the benefit of reducing emissions and improving engine performance: a higher compression ratio (CR) leads to an increase in fuel consumption and lower CO_2 emissions, while a lower CR during cold-start helps with higher exhaust temperatures for early catalyst light-off and lowers particulates due to reduced fuel impingement on the piston.
5. PFI vehicles generate low PM emissions into the environment compared to GDI vehicles, but GDI vehicles provide effective fuel economy and low greenhouse gas emissions because direct fuel injection technology can more accurately control the fuel volume and injection timing.

Conflicts of Interest

There was no potential conflict of interest on this research.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.csite.2019.100417.

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Chapter 5: Paper 4

Characterization of Ugandan biomass wastes as the potential candidates towards bioenergy production

This chapter reports the characterization of the new LCB material such as pretreated *Mbwazirume* peel (MP) and *Nakyinyika* peel (NP) biomass using various analyses such as proximate and ultimate, TGA, FT-IR, AAS, and SEM-EDS. This was in order to assess their suitability for bioenergy application in Uganda. The article has been published in the *Renewable and Sustainable Energy Reviews*, ELSEVIER BV.
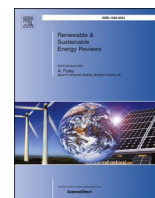
Characterization of Ugandan biomass wastes as the potential candidates towards bioenergy production

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ABSTRACT

Biomass waste can be characterized to identify its use in bio-energy production. This study aimed to characterize *Mbwazirume* peel (MP) and *Nakyinyika* peel (NP) biomass using various analyses such as proximate and ultimate, TGA, FT-IR, AAS, and SEM-EDS. This was in order to assess their suitability for bio-energy application in Uganda. Results indicate that MP biomass shows higher VM 69.988%, FC 13.582%, ash content 5.825%, and HHV 18.28 MJ-kg^{-1}, and shows lower moisture content 10.605%, nitrogen (N) 5.78%, oxygen (O) 46.74% and sulfur 0.30%. The decomposition of hemicellulose mainly takes place at 100–250 °C, cellulose at 300–500 °C, and lignin at 500 °C and above. The spectrometer results exhibit various functional groups which are related to C=C, OH, C=O, and C–O–C. The heavy metals (HMs) results for both samples indicate that Cu, Cd and Pb were low, and Zn was high. These toxics may not affect the environment due to their low amount of eco-toxicity and bioavailability. The SEM images show the presence of starch granules and irregular particles with heterogeneous morphology. This might justify the occurrence of high cellulose content due to additional restrictions on molecular motion. During the EDS analysis, the elements found in both ash residues were ordered as follows: O > K > C > Cl > Mg > P for MP, and K > Cl > Mg > P > Al for NP. All these properties proved that MP biomass is more suitable as a potential application for bio-energy.

1. Introduction

Banana is among of the most consumed fruits in the world, yet there is little industrial use for its peel, which constitutes 30%–40% of the weight of the fruit [1]. Uganda is ranked the second largest producer of bananas at 11.1 m tons per year, after India with 29.7 m tons of bananas produced per year [2]. Uganda is the number one consumer of bananas at 240 kg per capita per annum [2]. This means that bananas are key part of many families' everyday diet, which in return generates considerable quantities of banana peels each day all year round [3]. There are different types of bananas grown in Uganda for food consumption. These have been classified as green bananas (*Matooke*), plantain, and yellow or sweet bananas [1]. *Matooke* (*Musa-AAA-EA*) is a variety of banana indigenous to Uganda, which is the most essential staple food crop for human consumption. It comes from the family of bananas known as East African highland bananas. It appears to be green in color and thick at the midsection [4], and cannot be peeled in the same way as yellow bananas. These peels are used as animal feed or as local briquettes.

Despite the usage, about 61.8 kg per capital per annum of *Matooke* peels produced in Uganda become waste, due to the lack of sufficient structure and indiscriminate dumping. This huge amount of waste leads

to environmental health problems, and releases greenhouse gasses (GHG). Utilization of these types of wastes might differ from one country to another. For instance, in Cost Rica, it is common practice that the peels and rotten bananas are disposed of in the rivers which decreases the populations of aquatic animals causing an imbalance in the ecosystem [5]. In previous years, Brazil utilized banana peel as a local and traditional medicine to protect a wound from swelling [6], and Satyanarayana [7] utilized its peel for polymer composites. However, these peels are lignocelluloses biomass (LCB) which contain more than 70 wt% of carbohydrates [1,8], which make these peels suitable for bio-energy production using several biotechnological techniques [9]. These techniques include physical and chemical, thermo-chemical, and bio-chemical conversion [10]. In addition, utilizing *Matooke* biomass waste for bio-energy in Uganda might help to minimize conventional fuel dependency and eliminate environmental pollution.

LCB has a complex matrix rich in high-value compounds [5], mainly made up of cellulose, hemicellulose, and lignin [11]. As reported in the literature, bio-energy produced from LCB can be used as a replacement for gasoline fuel [1]. However, challenges still remain, such as the small differences in biofuel properties that are enough to create a significant behavior in the combustion system [12]. These variations occur because of the variation in lignocelluloses properties and the degree of polymerization, particle size, extraction process [13], molecular weight and structure, and thermal stability behavior [14]. Various techniques have been utilized to characterize the properties of LCB. They include crystallinity, which is an essential biomass property (analyzed using FT-IR or X-ray diffraction) [15], thermal and volatiles (analyzed using thermogravimetric analysis TGA) [16], heavy metals (analyzed using atomic absorption spectroscopy AAS) [17], and surface morphology and elements (analyzed using scanning electron microscopy SEM and energy dispersive X-ray spectrometer EDS) [18,19].

This research aimed to characterize LCB from two varieties of *Matooke* peel biomass, namely, *Mbwazirume* (MP) and *Nakyinyika* (NP), as potential candidates for bio-energy production. This characterization will provide insight regarding what is likely to occur in biotechnological processes, and in terms of the combustion performance of spark-ignition (SI) engines. Though some researchers have carried out on characterization of banana peel [19–23], no published literature is available on characterization (such as TGA, FT-IR, AAS, and SEM-EDS) of *Matooke* peel biomass for its use in production of bio-energy.

2. Material and methods

2.1. Sample preparation

MP and NP were obtained (in bulk) from different locations in Uganda. The peels were removed using a sharp knife, and then washed thoroughly with distilled water to remove the physical adsorbed contamination. The two species were dried at 48 °C for a period of 83 h–95 h as described in previous article [1].

2.2. Characterization of Matooke peel samples

Various techniques have been used to characterize the effects of LCBs. These characterization analyses include: proximate, ultimate, thermogravimetric, FT-IR, SEM-EDX, and heavy metal analyses. The biomass samples in this study had a particle size of 0.2 mm after grinding (using DIN 51704 standards) because high-energy output depends on the particle size and reduction in crystallinity of the LCB. The ground
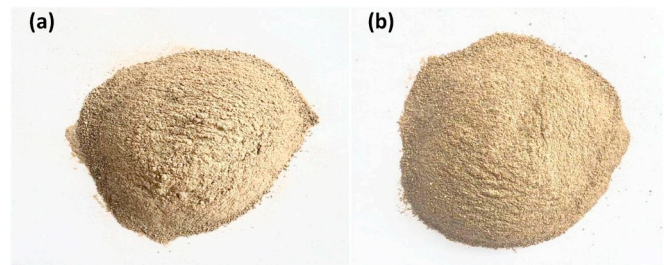
Fig. 1. The grinded LCB samples: (a) MP, and (b) NP.

LCB samples are shown in Fig. 1(a–b), with both samples having the same color. Preparing the sample is a key aspect of the methodology, and different LCBs require different methods. Solid fuels are analyzed by the following standards procedures: ASTM and DIN, which were presented and described by DIN 51718–20 [24]; ASTM E775-78 [25]; ASTM E1252-98 [26]; and ASTM D3335-85a [17]; and SEM-EDX by Ref. [19].

2.2.1. Proximate analysis

This proximate analysis was to determine the major components of the biomass, namely: moisture content (MC), volatile matter (VM), fixed carbon (FC), and ash content. In this analytical process, the MC was determine using the DIN 51718 standard in which 1 g of each of the biomass samples were weighed on two different dried aluminum dishes and placed in a furnace at a temperature of 105 °C ± 1 °C for 3 h. After the heat process, the MP and NP were withdrawn from the furnace and allowed cool [27]. The moisture content of biomasses were determined based on the initial weight of the MP and NP before heat treatment (M_i), and the final weight of the MP and NP after heat treatment (M_f), which was recorded.

The VM content of the biomasses were determined according to the DIN 51720 standard. This test was carried out by heating the samples at a temperature of 919 °C for 7 min with a heating rate of 10 °C min^{-1} under N_2 atmospheric conditions, followed by cooling at ambient temperature. The percentage reduction in weight of the samples was determined using the TGA integrated program. As the weight loss is directly proportional to VM, the VM content was determined when the weight loss (minus moisture) at 1 g of sample was heated to 919 °C for 7 min.

The DIN 51719 standard was used to determine the weight of the ash. At a constant weight, the MP and NP were placed back into the furnace and gradually heated to 750 °C for 1 h. The aluminum dishes with the samples were withdrawn from the furnace and allowed to cool at ambient temperature in a desiccator.

2.2.2. Ultimate analysis and higher heating value (HHV)

Ultimate analysis was used to determine the elemental composition of the MP and NP samples using PerkinElmer 2400 Series II which has the capability of adjusting the temperature to a maximum of 1100 °C. The elements such as C, H, O, N and S were determined using ASTM E775-78 standards in which (1.00 mg–2.00 mg) of the samples on a dry basis were placed inside a muffle furnace. These elements were analyzed during the simultaneous combustion of the gases. Besides, the HHV can be calculated once the elemental composition is known. In this analysis, the HHV was determined using the known elemental composition (as determined in ultimate analysis) with equation (1), which is acceptable for engineering calculations [28]:

$$HHV = 0.3491x(\%C) + 1.1783x(\%H) - 0.1034x(\%O) + 0.1005x(\%S) - 0.0151x(\%N) - 0.0211x(\%Ash)[MJ/kg] \quad (1)$$

2.2.3. FT-IR analysis and thermal analysis

The spectrums of the MP and NP biomasses were obtained from Nicolet 6000 FT-IR. The biomasses were scanned between the wavelengths of 400 cm^{-1} and 4000 cm^{-1} with a resolution of 4 cm^{-1}. The spectra data generated were analyzed using irAnalyze-PAMalyze 4.0 software and the organic functional groups present in the samples were characterized, as presented by Ref. [26].

TG-DTG analyses were carried out on two biomass samples with a TGA thermostep analyzer by ELTRA, Germany. To avoid heat and mass transfer restrictions, small portions of the biomasses (5 mg and 10 mg) were used as described by Ref. [29]. The two samples were prepared and heated from ambient temperature to 1000 °C at 10 °C min^{-1} under nitrogen atmosphere [26]. Heating rate, weight loss, moisture, volatile, ash content, and fixed carbon were recorded for both biomass samples.

2.2.4. AAS and SEM-EDS analyses

This analysis was determined using PerkinElmer AAnalyst AAS, to determine the HM (Cu, Pd, Zn, and Cd) content of the samples using the ASTM procedure. The biomass samples were weighed (5 g) and transferred into tarred crucibles. These samples were placed in a cool furnace and ignited for 4 h–6 h at 550 °C. After the required time, the muffle furnace was turned off and the samples were left inside until the temperature dropped down. The ash samples were dissolved in 1:1 (5 ml nitric acid: 5 ml distilled water); and the solution was warmed so that any un-dissolved particles and residue could dissolve. The solutions were filtered using filter paper into a 50 ml volumetric flask. The AAS analysis method and protocol followed the ASTM D3335-85a (2014) procedure [19], and the UIRI/QMP/07 method as modified by the Uganda National Bureau of Standards (UNBS) for the Uganda Industrial Research Institute (UIRI) specific equipment.

During SEM-EDS analysis, the SEM (VEGA 3 TESCAN- LMH) was used to determine the micro-structural behavior of the MP and NP samples (coated with a thin layer of carbon) at 50/60 Hz, 230 V and 1300 VA, coupled with EDAX to determine the elemental composition.

3. Results and discussion

3.1. Proximate analysis

The proximate and ultimate composition of MP and NP are shown in Table 1. In terms of proximate composition, the percentage content of MC, VM, FC, and ash obtained from MP and NP were in the range within the literature as presented by Ref. [20]. An analysis of the data reveals that MP has a low moisture content compared to NP. This trend may be attributed to the ambient temperature of the procedure used as reported in section (2.2.1). On the other hand, the variation of MC in these samples could be related to the fact that upon fruit ripening, the MC of the plant fiber decreases due to the climate changes and the heat from sun drying [30]. It is suggested that high moisture content may lead to reduction in burning capacity, and low moisture content will mitigate the problem of poor ignition related to the combustion of biomass fuels.

A large content of VM (69.988 wt%) and (69.980 wt%) was identified in the MP and NP peels, which represents about 75% of the fuel. This VM contents is relatively high compared to other biomass fuels (as presented in the literature) such as oil palm fiber with 65.75 wt% [31]
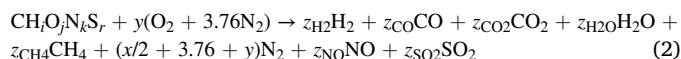
and rice husk with 65.33 wt% [32], but lower than that of flax straw with 78.8 wt% [33], and *Eragrostis airoides* with 86.84 wt% [27]. The ignition of such high volatile fuels may lead to high flame length unlike low volatile fuels which ignite less readily. Besides, the higher the volatile content in a fuel, the higher the HHV and the less heat is required for the thermochemical reactions [34].

Ash is an undesirable constituent in fuel. In this context, the ash content within the samples shows a very interesting phenomena, falling between 4.773 wt% and 5.825 wt%. These contents are lower than the results obtained by Ref. [35] for corn stover, by Ref. [32] for rice husk, by Ref. [36] for wheat straw, similar with [37], but higher than those obtained by Ref. [38] for oil from palm shells. As reported in the literature, any biomass with an ash percentage less than 5%–6% does not undergo knocking trends [39]. Thus, the biomass wastes MP and NP can be classified as cleaner fuels due to their low ash content.

The FC is the content of ash-free carbon which remains after the release of VM. The percentage of fixed carbon in MP and NP were found to be 13.582 wt% and 12.879 wt% respectively. This indicates that MP shows a slightly higher percentage of FC compared to NP and other biomass fuels reported for pinewood and barley strew by Ref. [40], spruce by Ref. [41], and peach bagasse by Ref. [42]. Yang et al. [43] reported that the FC content in biomass fuels is expected to vary in a range of 7%–20%. The relation between cellulose and lignin contents with FC was observed in these results, indicating that the higher the cellulose the larger the FC. Hence, biomass with a high cellulose and FC content is likely to have high fiber content [44]. This is among the variables used to obtain the efficiency of solid fuel combustion.

3.2. Ultimate analysis

In this study the ultimate analysis of biomass fuels was accomplished through being decomposed in a simultaneous combustion, in which (C, H, O, N and S) reacts with the exothermic reaction process and generates CO_2, H_2O, NO_x, and SO_2 respectively [45]. This decomposition of biomass fuels occurs in the form of equation (2):

$$CH_iO_jN_kS_r + y(O_2 + 3.76N_2) \rightarrow z_{H2}H_2 + z_{CO}CO + z_{CO2}CO_2 + z_{H2O}H_2O + z_{CH4}CH_4 + (x/2 + 3.76 + y)N_2 + z_{NO}NO + z_{SO2}SO_2 \qquad (2)$$

As reported in Table 1, the ultimate composition of MP and NP peels found in this study are slightly different. The contents of C, H, and O in MP are relatively high, and lower in N and S content than other biomass fuels. As presented in the literature, a decrease in H and O content in the biomass fuels can be associated with the scission of weak bonds within the char structure [46]. The percentage of S and ash content is low in both biomass samples, which shows they are good candidates for biofuel production compared to coal with 0.5%–7.5% [28], and other biomass wastes presented by Refs. [16,31,38]. In addition, it is suggested that this biomass waste does not need any processing or technology for reducing the exhaust emission of sulfur oxides (SO_x) and nitrogen oxides (NO_x), since the S and N contents are relatively low. However, C and O is directly proportion to the fuel's HHV. The HHV or calorific value is a parameter that determines if the biomass qualifies to function as a fuel. The calorific value of MP and NP obtained were 18.28 MJ-kg^{-1} and 17.76 MJ-kg^{-1} respectively; this may be a significant for production of bio-energy.

Table 1
Proximate and ultimate composition of MP and NP biomass.

Samples	Particle size (mm)	Proximate analysis				Ultimate analysis					HHV* (MJ-kg^{-1})
		MC	VM	Ash	FC	C	H	N	O	S	
		(wt. %)				(wt. %)					
MP	0.2	10.605	69.988	5.825	13.582	46.94	5.79	0.23	46.74	0.30	18.28
NP		12.368	69.980	4.773	12.879	46.22	5.60	0.41	47.41	0.36	17.76

Note: * calculated HHV (MJ-kg^{-1}).
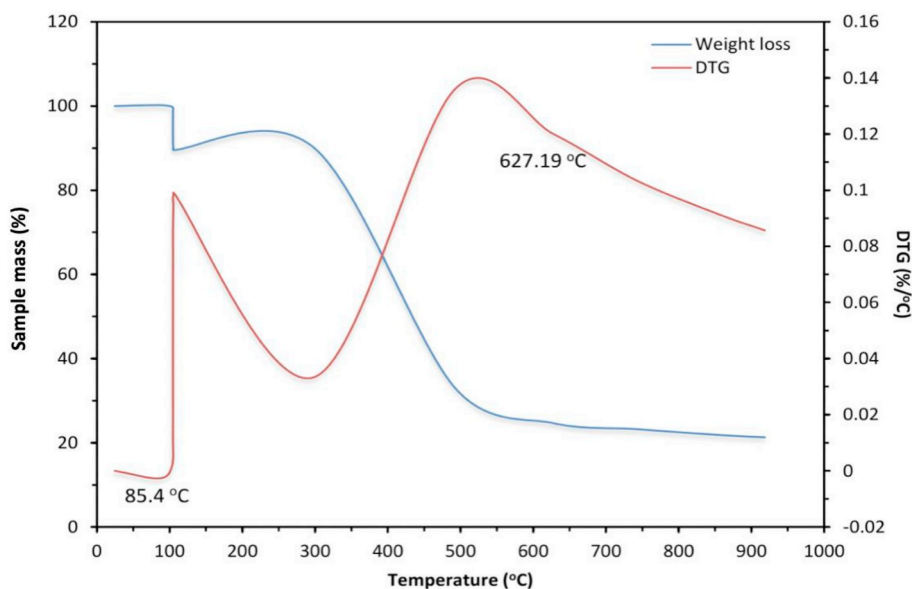
Fig. 2. TG-DTG curve of MP.
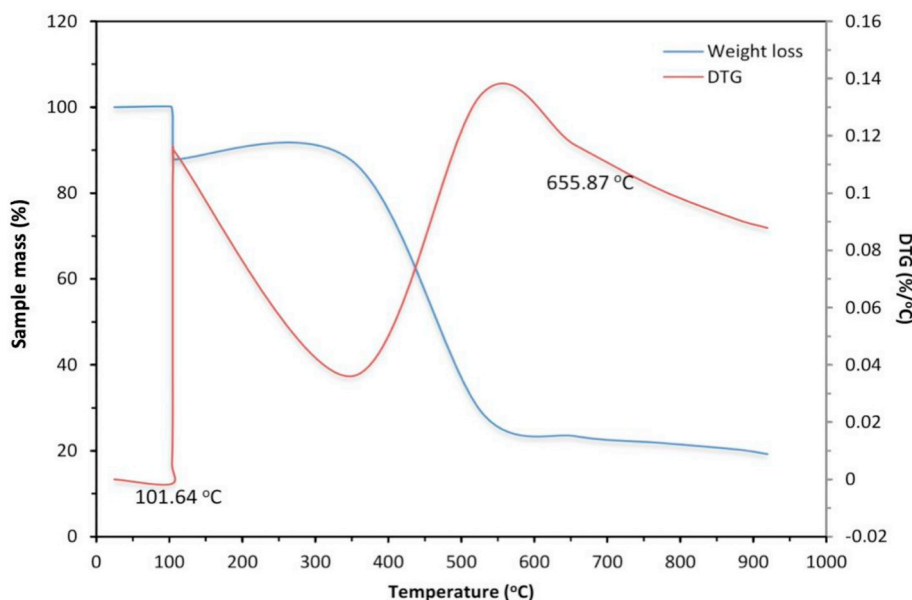
Fig. 3. TG-DTG curve of NP.

3.3. Analysis of thermal properties

The TG-DTG curves of biomass samples MP (Fig. 2) and NP (Fig. 3) were determined. According to the thermal results obtained, three distinct regions are clearly identified at temperature up to 900 °C, which is related to elimination of cellulose, hemicellulose and finally lignin. These occur as a result of three steps in weight loss during the thermal degradation: water removal (drying), organic matter release (devolatilization), and bonded-carbon oxidation (slow combustion). The pyrolysis decomposition peaks of LCB samples in nitrogen atmosphere occurred at elevated temperatures as follows: hemicellulose (100 °C–250 °C), cellulose (300 °C–500 °C), and lignin (500 °C–650 °C). There was very little weight loss in the range 50 °C–70 °C because the samples were not fully dried yet due to the presence of humidity. Figs. 2 and 3 show that from 300 °C upwards did a meaningful weight reduction due to the pyrolysis of the biomass. The degradation of the biomasses at

(>570 °C) were observed as a result of the breaking of bonds of the *protolignin* (lignin present in the samples), as presented by Refs. [37,47].

Table 2 reveals the thermal behavior results of MP and NP samples from TG-DTG at a heating rate of 10 °C min^{-1}. It needs to be pointed out that the composition of LCBs can vary, even within the identical species and varieties, which causes the thermal pyrolysis behavior to be

Table 2
The thermal behaviors of MP and NP biomass from TG- DTG scan.

LCBs	T_{idt} (°C)	Temperature during change in sample mass (°C)	Sample mass (%)	Residual char at 919 °C (%)	Maximum change in sample mass with respect to time (°C min^{-1})
MP	85.4	627	75.33	0.2406	0.615
NP	101.6	655	76.59	0.2147	0.620

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dissimilar, although in this study the DTG of the LCBs has some similar behavior in the same ranges mentioned. The maximum change in sample mass was about 0.615% min^{-1}, which corresponds to a peak temperature of about 627 °C. At this point, the sample mass was about 75.33% (Fig. 2 and Table 2). As shown in Table 2, NP exhibited a 76.59% sample mass at 655 °C with maximum change in sample mass of 0.620% min^{-1}; this trend is due to endothermic effects. In addition, the TG-DTG curves showed the presence of change in sample mass with corresponding temperatures. MP showed an obvious decrease during the exothermic reaction, confirming the presence of a few organic compounds which were exothermic.

As shown in Table 2, the initial decomposition temperature (T_{idt}) obtained from the TG-DTG results indicate that the thermal rationality for both biomasses were ordered as follows: MP > NP. At 919 °C, the residual char of MP presents the highest content, which is associated with a high percentage of lignin compared to NP. The content of residual char in the TG-DTG is the remaining composition after all volatile products have been wiped away during thermal decomposition; lignin was the major ingredient of the residual char and is associated with complex and thermally stable structures [30].

3.4. FTIR analysis

The FT-IR shows that the absorption peaks of MP (Fig. 4) spectra were significantly lower than the absorption peaks of NP (Fig. 5), but similar in range. This reveals that the stretching band appears to a lesser degree, which can be attributed to the interaction of metals (Cu, Cd, Cr, Zn, and Pb) which substantially reduce absorption. This finding is in agreement with the results obtained by other researchers [48–50]. Both infrared data indicate miscibility of the bends, which are related to hydrogen bonded stretching between the reactive functional groups in lignin with the carbonyl groups. Fig. 4 shows that the peak range of carbonyl (C=O) is 1740 cm^{-1} to 1710 cm^{-1}, which is decreased at absorption compared to that of Fig. 5, while the broad C=O stretching vibration is very strong. The literature indicates that oxygenates are characterized by the presence of a carbonyl group in their respective molecular structures [51], as evident in the spectra shown in Fig. 4, which shows large contents of alcohol, alkenes and alkyl groups compared to the other LCB as shown in Fig. 5. Most of these groups are classified as potential biofuel candidates [52].

The peak frequency of 3450 cm^{-1} to 3300 cm^{-1} range is associated with variable absorption of (OH) stretch in hydroxyl groups; this indicates a high-energy region with large content (≥70%) of carbohydrates (lignin and cellulose) in the samples, while the broad peak in the

range of 2975 cm^{-1} to 2840 cm^{-1} shows the presence of stretch bonds between atoms C–H in the form of CH_2 symmetry. This contribution was observed for all the samples. Further, the wave of 1135 cm^{-1} to 1080 cm^{-1} in both samples shows the presence of ether aliphatic through stretching bonds of C–O with strong intensity, as presented by Ref. [53]. In Fig. 4, the spectra revealed a higher onset and peaks of other monomers in the range of 2950 cm^{-1} to 2803 cm^{-1}, which are higher than that of Fig. 5. This trend is due to the presence of electrons that are linked with some ether; the increases in ether chain length may cause an increase in electron density, which decreases the curing temperature [54,55].

The results in Fig. 4 show 100% of the contents of molecular structures such as N-methylaniline monomethylaniline, nitrosodiphenylamine, and 4-sec-butyl-phenylenediamine. The absorption wave of 1665 cm^{-1} to 1620 cm^{-1} range in both samples shows the presence of an alkene group with high C=C bonds, indicating a biomass constituent being oxidized (lignin) due to its high content of C=C bonds [56]. The challenge as a result of oxidation is the formation of free radicals. When the oxidation degradation between the double bonds occurs at the saturated carbon, the isomerization stabilizes within double bonds to form conjugated structures [57]. This then generates a mechanism which interacts with oxygen to establish peroxide species, and eventually decreases the fuel qualities and leads to plugged filters and degraded combustion rector and fuel-line components [57].

3.5. Distribution of HMs in biomass wastes

3.5.1. The HMs and its effects

The evaluation of quantitative HMs contents such as Cu, Cd, Zn, and Pb in biomass samples is shown in Table 3 using the ASTM D3335-85a (2014) standards. The objective of this analysis was to determine the HMs content in the samples and relate it with the previous literature on how this may affect the environment and bio-energy production in future. HMs are associated with the combustion of fuels, and spread through air to the soil and to surface water. A lot of transportation vehicles and fuel production industries produce and discharge exhaust pollution containing different HMs. The heavy metal pollution are metals that have a specific density of more than 5 g/cm^3 [58], which affects the environment and eco-system. Naturally, the body requires very small amounts of HMs for maintaining good health but if they are too high they become toxic and dangerous to human health [58]. The amount of HMs in emissions through biofuel combustion has a strongly relation to the HMs content in dried biomass fuels.

As shown in Table 3, MP shows low values in Cu (0.2660 mg-kg^{-1}),
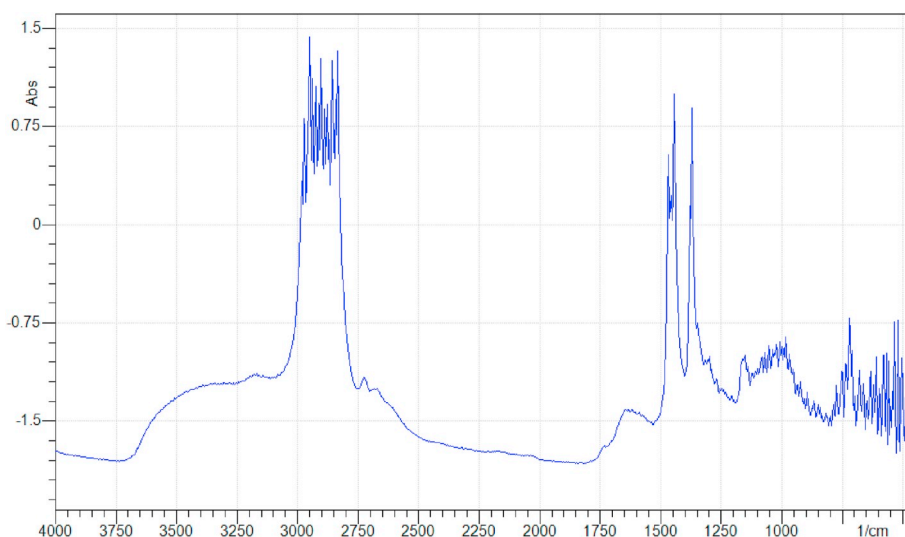

Fig. 4. The FT-IR spectra of MP.
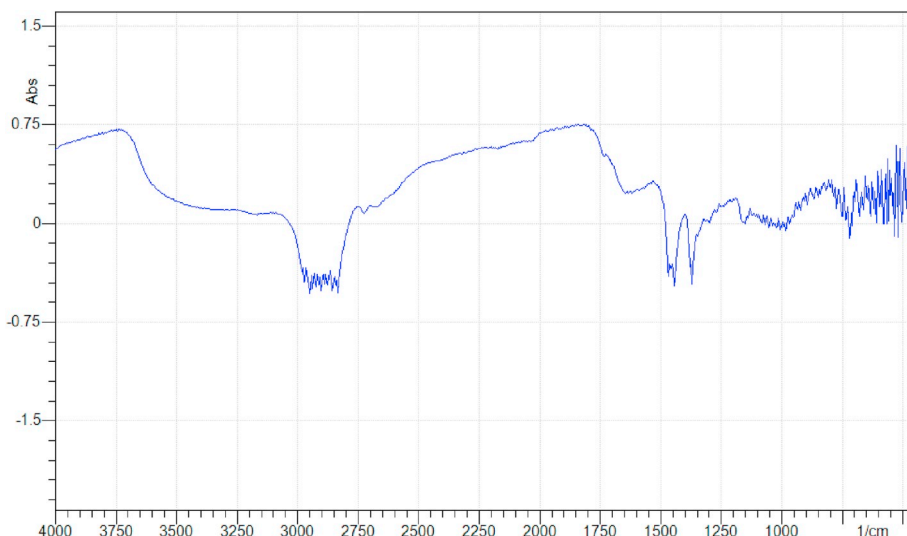
Fig. 5. The FT-IR spectra of NP.

Table 3
The composition of HMs in biomass samples.

Samples	Heavy metals (elements)	Values found (mg/kg)	Concentration (ppm)	Absorbance from AAS
MP	Cu	0.2660	0.027	0.034
	Zn	7.3537	0.746	0.673
	Cd	1.0032	0.102	0.010
	Pb	1.6154	0.164	0.271
NP	Cu	0.2687	0.027	0.038
	Zn	7.3239	0.745	0.672
	Cd	1.0699	0.109	0.032
	Pb	1.6503	0.168	0.275

Fig. 6. Residual rate of HMs in MP and NP.

Cd ($1.0032 \, \text{mg-kg}^{-1}$), and Pb ($1.6154 \, \text{mg-kg}^{-1}$) with a slightly high value of Zn ($7.3537 \, \text{mg-kg}^{-1}$), compared to NP; this may occur due to dilution effects. The fraction of HMs in both biomasses indicates that Cu, Cd, and Pb were low, and these are the main HMs, but due to the low values they may not affect the environment in terms of eco-toxicity and humans in terms of bioavailability [59], and will have zero effects on bio-energy production. The contents of Cu, Cd, Zn, and Pb in all the biomasses shows a very low trend compared to studies on rice straw and sawdust by Ref. [60], and white wood by Ref. [61]. It was reported that most of the HMs such as Cu, Cd, Zn, and Pb in biomass endure the pyrolysis residue process at temperatures up to 705 °C [62,63]. However, this was resolved by Refs. [64,65] they introduced the process of evaluating and leaching this effect of HMs, which possibly reduces the influence of environmental pollution hazards.

3.5.2. The percentage rate of HMs

The percentage rate (P_1) of HMs in MP and NP has been suggested as a gauge for evaluating the amount of Cu, Cd, Zn and Pb through AAS results. P_1 is defined as the ratio of the content found of each HM to the total contents of HM in the LCB. The percentage rate can be calculated as follows:

$$P_1(\%) = \frac{CF_Z}{TC_Z} x \, 100 \tag{3}$$

where Z represents the type of HM; CF_Z the content of HMs found in the residue (mg/kg) (Table 3); and TC_Z the total content of HMs in the residues (mg/kg) [64]. As illustrated in Fig. 6, the percentage rate of Zn in MP and NP were all over 70%, which indicated that the two biomass fuels had a high percentage rate of Zn compared to the other elements

found. Although Zn is slightly less effective [66].

3.6. SEM-EDS analyses

SEM-EDS is an essential technique used to examine micro-scale and nano-scale behaviors and detect the chemical elemental composition which occurs during thermal degradation of the biomass. As presented in micrographs Figure 7(a-b), irregular particles with heterogeneous morphology and starch granules were present; the surface morphology was taken at magnifications of 500×, which gives 100 μm. These images confirm the presence of high fiber content, and clearly demonstrate the presence of high cellulose content (as explained in section 3.1). These trends are due to the additional restrictions on molecular motion [67, 68]. As shown in Fig. 7(a), the residual cell structure of the samples is clearly visible, indicating the fibrous buildup inside the carbon structure. From Fig. 7(b) it can be observed that the structures seem to behave independently in some parts. This might cause the NP biomass to burn faster than MP during combustion. As previously reported by Ref. [69] the combustion reactivity of a biomass directly relates to the char morphology formed.

Small white spots appear in both biomass samples Fig. 7(a–b) which are elements from various categories: non-volatile such as magnesium (Mg), Aluminum (Al); and volatile such as chlorine (Cl), potassium (K), phosphorus (P); and C and O (as shown in Fig. 7(c–d)). These elements were in the oxidized state and may experience fusion occurrence. This
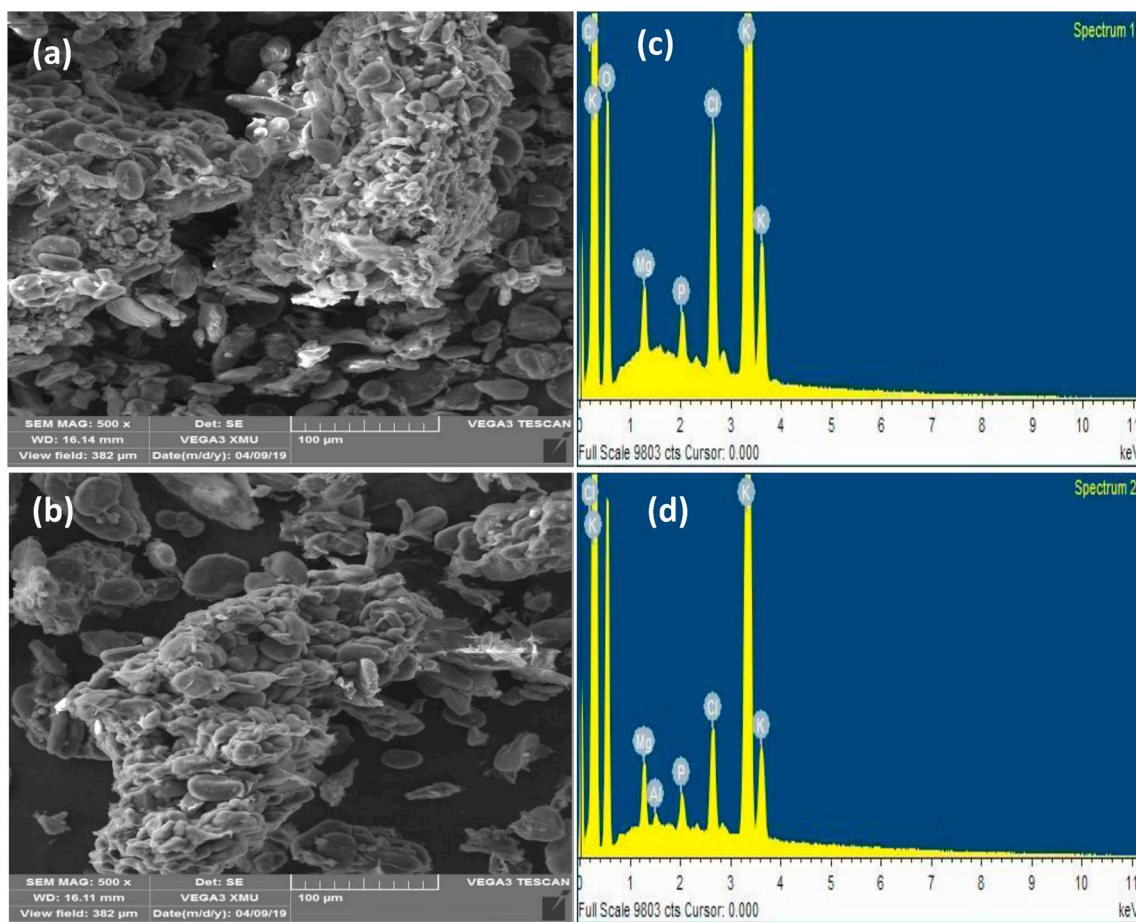
Fig. 7. (a–b) SEM images of MP and NP; (c–d) EDS spectrum of MP and NP.

was consistent with other results on rice husk and wood by some authors at temperatures from 800 °C to 1000 °C [70,71]. However, large contents of mineral parts occurred on the surfaces of the particles that were pyrolyzed at the highest temperature (~1000 °C). This higher content of inorganic components in the residue is associated with a higher consumption of organic matter during the reaction [72]. Moreover, some of the particles appeared to be heterogeneous at residence time of 0.5 s–0.7 s, and conserved a fibrous form and molten coating on some parts.

As shown in Table 4 and Fig. 7(c–d), the elements found in both ash residues were ordered as follows: O > K > C > Cl > Mg > P for MP, and K > Cl > Mg > P > Al for NP. During the EDS analyses, it was observed that the samples were typically rich in K, Cl, Mg, and a trace of P. These findings regarding the elemental ash composition of the biomasses varies compared to the literature reported with other biomass which have higher contents of C [19], Cl and N [73], but coincide with the contents of K by Ref. [74]. In this study, the K and Cl are often present in both samples' ash composition at low melting temperatures. This suggests that during the gasification process, the high temperature combustion (>700 °C) eliminates the corrosive ash compositions (K and Cl)

that might cause troublesome in the future. This may be a useful result for bio-energy production.

3.7. Practical and policy implications

The increase in demand and identifying the resources for energy are key issues for most countries in Africa. For instance, in Uganda, electricity distribution is one of the lowest in Africa; estimated at only 22% of the total Ugandan population and dropped 8–10% in rural areas. Besides, the country is highly vulnerable to oil price shocks as it imports almost all of its 31,490 barrels per day (5006.5 m^3/d) of oil from Kenya [75]. These makes the energy consumption from transportation sectors become problem. Such limited and unreliable energy access translates into underutilization of the excessive biomass (*Matooke* peels) wastes which are renewable and sustainable sources for bioenergy production [12]. These challenges have led to practical and policy implications in Uganda focusing on energy consumption management and alternative sources for biofuel which are stringent necessity, both to meet the energy demands, increase in efficiency, and GHG emissions [76].

The main objectives of energy-related policies in Uganda are as follows: 1) diversify the modern renewable energy sources and technologies; 2) develop the energy needs in an environmentally sustainable way; 3) establish the petroleum potential and promote its exploitation; 4) promoting local and national policy efforts on environmental issues [77–79].

With the above background and policies presented in Table 5, it is found that the renewable energy policy (REP) 2007 was the appropriate policy for this research finding. Although not all biomass bring benefits to the environment, assessment needs to be made for each type of LCB, location, and the extraction methods. This will help in identifying the

Table 4
EDS analysis of elemental ash composition for MP and NP biomass.

Samples	Elements						
	O	C	Mg	Al	P	Cl	K
	(wt.%)						
MP	37.34	24.47	1.98	–	1.41	4.66	30.14
NP	–	–	5.40	0.65	3.14	9.58	81.22

Table 5
Problems and implications of energy-related policies in Uganda.

Policies	Year	Policy objectives	Problems	Implications
National environment management policy (NEMP)	1994	To harmonize local and national policy efforts on environmental issues.	• Uganda imports all its petroleum products requirements from Kenya since local production has not yet been established.	• Ugandan government must introduce the use of alternative fuels, e.g. bioethanol production from *matooke* peels biomass which is significant.
National energy policy (NEP)	2002	Promoting the energy necessity of Uganda's population for social and economic development in an environmentally sustainable manner.	• Insufficient data available on the potential of indigenous renewable energy sources.	• Ugandan government must formulate a database on all the accessible energy resources (e.g. *matooke* peels biomass) and energy consumption patterns.
Renewable energy policy (REP)	2007	To diversify the modern renewable energy sources and technologies in the country.	• GHG emissions from vehicles also constitute a significant portion of pollutants in Uganda.	• Ugandan government must introduce a legislation, which will obligate petroleum companies to blend gasoline fuels with certain percentage of biofuel. This biofuel will be used mainly, in the transport sector (to reduce the energy-related emissions that are harmful to the environment) and for power generation.
National oil and gas policy (NOGP)	2008	To establish the petroleum potential of the country and to promote its exploitation.	• Inadequate and inefficient power supply system. • Budgetary constraints. • There is limited awareness of the availability, benefits and opportunities of renewable energy.	• Ugandan government must enact laws to control disposal of biomass wastes, without extracting the energy content of the biomass. This measure will increase the energy available for use and reduce further deforestation. • Ugandan government must facilitate adequate financing schemes for RETs by establishing sustainable financing mechanisms to make them more accessible. • Ugandan government must involve private and public partnerships in the formulation of new policies in the energy sector. • Ugandan government need to encouraged sector reform to integrate the act of sub-sectors. This will help to define action plans in a more focused manner.

opportunities for reaching Ugandan bioenergy's targets over a medium to long term, since bioenergy can be used for many purposes such as generating electricity and as well as transportation fuel.

4. Conclusion

The data from proximate, ultimate and thermal analyses found that MP biomass exhibits excellent properties when compared to NP and other biomasses reported in the literature. The spectrum shows different behavioral structures of the absorption peaks, revealing that the stretching band occurs to a lesser degree due to the interaction or to small amounts of HMs in the biomass waste. In MP spectra, it was observed that the absorption was associated with a high content of aliphatic and aromatic hydrocarbons, alcohol functional groups, and molecular structure such as *N*-methylaniline monomethylaniline, and 4-*sec*-butyl-phenylenediamine than NP.

The presence of HMs in the biomass samples, such as Cu, Cd, Zn and Pb, probably have no effect on the bio-energy produced and environment. However, Zn requires attention due to the presence of a moderate threat to the environment under certain conditions. The micrographs show the presence of starch granules and irregular particles with heterogeneous morphology; these results cause the oxygen to easily disperse inside the particles during combustion. In EDS analysis, white spots were observed which are elements from different categories.

Declarations of interest

None.

Acknowledgment

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Chapter 6: Paper 5

Comparative Study on Pyrolysis and Combustion Behavior of Untreated *Matooke* Biomass Wastes in East Africa via TGA, SEM, and EDXS

This chapter characterizes the unique biomass from the variety of *Matooke* peel which is untreated *Mbwazirume* waste peel (UM-WP) and untreated *Nakyinyika* waste peel (UN-WP). It is suggested that this exploration can be added to the biomass database as an alternative energy source. The article has been published in the *International Journal of Energy and Environmental Engineering*. SPRINGER NATURE.

ORIGINAL RESEARCH

Comparative study on pyrolysis and combustion behavior of untreated *Matooke* biomass wastes in East Africa via TGA, SEM, and EDXS

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Abstract

Biomass has several benefits due to its novel behavior among energy sources. This study aims to characterize a unique form of biomass from two varieties of *Matooke* peel, namely, untreated *Mbwazirume* waste peel (UM-WP) and untreated *Nakyinyika* waste peel (UN-WP). The analysis of the characteristics of these biomasses was carried out using TGA, SEM, and EDXS. TG and DTG analysis showed an almost identical trend between UM-WP and UN-WP. The UM-WP exhibited a high VC 69.988 wt%, MC 13.125 wt%, O 48.02 wt%, and HHV 15.52 MJ-kg^{-1} with a low ash content 5.957 wt%, sulfur 0.64 wt%, and N 1.13 wt% compared to UN-WP. As compared to pretreated biomass, it was found that the smaller particle sizes had only minor intra-particle gradients and the bigger particle sizes had more of a linear pattern variation. The pyrolysis behavior obtained revealed three distinct regions at elevated temperatures related to the elimination of cellulose, hemicellulose, and lignin. During carbonization, high fluidity and bubbles were produced due to the release of a large amount of volatile matter and forms porous structure which flowed through the fluid mass and produced a non-homogeneous vacuolated structure. These might cause the oxygen to easily disperse inside the particles during combustion. In addition, white spots were observed which are elements from different categories. The findings of this study indicate that UM-WP biomass could be an ideal material source for the production of biofuel and photovoltaic.

Keywords Biomass · Energy · Intra-particle · Micrographs · Biofuel

Abbreviations

UM-WP	Untreated *Mbwazirume* waste peel
UN-WP	Untreated *Nakyinyika* waste peel
TGA	Thermogravimetric analysis
SEM	Scanning electron microscopes
EDXS	Energy-dispersive X-ray spectroscopy
FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffraction
HHV	Higher heating value
MP	*Matooke* peel
VM	Volatile matter
FC	Fixed carbon
MC	Moisture content
LCB	Lignocellulosic biomass

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Introduction

The increase in demand for energy and identifying appropriate resources for energy production are key issues for most countries in the Africa. For instance, Uganda is highly vulnerable to oil price shocks in East Africa, because it imports almost all of its 31,490 barrels per day (5006.5 m^3/day) of oil from Kenya [1]. This causes problems for the transportation sector. In addition, the country has one of the lowest per capita electricity consumption rates in the world with 215 kWh per capita per year [2]. Such limited and unreliable energy access represents an underutilization of the large amount of biomass waste available in the country. For this reason, more attention should be paid to renewable energy,

especially biomass energy, which is the case now in many countries [3, 4]. A number of different forms of biomass and waste can be used as fuels to be burned, digested, or co-combusted with coal to produce energy [5]. Examples of these energy sources include wood, straw, bagasse, *matooke* peels, agro-residues, municipal solid waste, etc.

Matooke (*Musa-AAA-EA*) is a variety of banana indigenous to Uganda, and is the most common staple food crop for human consumption in that country. It comes from the family of bananas known as East African highland bananas [6, 7]. The waste residue of *Matooke* is the peels, and a large amount of *Matooke* peel (MP) is generated every year; so, it is the most abundant agricultural biomass in East Africa, especially Uganda. This is due to the lack of sufficient structure to process this waste; so there is indiscriminate dumping, resulting in environmental pollution and loss of economic opportunities [8]. Although little amount of peel is used as animal feed and as local briquettes. Besides, biowastes of various origins are utilized despite the number of negative side effects they introduce to environment. This type of waste resource can be converted into energy recovery by means of thermochemical conversion processes, since it does not compete with the human food chain, and in turn improves the CO_2 balance [9].

The calorific values, high volatility, and fixed carbon contents indicate that this biomass waste could be an excellent energy source through various technologies such as combustion, gasification and pyrolysis [10]. Pyrolysis is a thermal and degradation technique performed under N_2 atmosphere [11], while combustion takes place under severe oxidative conditions with the aid of an ignition system. There are many reports on the effect of combustion and pyrolysis conditions on the physical and chemical properties of biomass. These properties of biomass char are generally characterized by thermogravimetric analysis (TGA), scanning electron microscopes (SEM), energy-dispersive X-ray spectroscopy (EDXS), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD).

The objective of this study was to characterize the unique biomass from two varieties of *Matooke* peel, namely, UM-WP and UN-WP with TGA, SEM, and EDXS. According to the available literature, there is only one published article on characterization of pretreated *Mbwazirume* and *Nakyinyika* biowaste [7]. Therefore, there is a need for additional experiments on pyrolysis and the combustion behavior of untreated *Mbwazirume* and *Nakyinyika* biowaste, and for comparison of the samples. The contributions from these various technological processes are described to verify the mechanism of combustion and thermal degradation of biowaste and visualize the feasible recovery of biofuels by means of the thermochemical conversion process.

Materials and methods

Characterization of UM-WP and UN-WP samples

These characterization analyses include: proximate, ultimate, TGA, SEM and EDXS. The biomass sample in this study had a particle size of 0.7 mm after grinding because high-energy output depends on the particle size and reduction in crystallinity of the LCB. The UM-WP and UN-WP samples are shown in Fig. 1a, b.

Proximate and ultimate analyses

The proximate and ultimate analyses are essential methods of characterization. The proximate analysis determines the composition of a biomass in terms of wt% of volatile matter (VM), fixed carbon (FC), moisture content (MC), and ash. In this study, these compositions were obtained according to ASTM standards (DIN 51718, DIN 51719, and DIN 51720). The method was that 1 g of each of the biomass samples was weighed on two different dried aluminum dishes and placed in a furnace at a required temperature under N_2 atmospheric conditions. For ultimate analysis, the chemical elements such as C, H, O, N and S were determined. The method was that 1.00–2.00 mg of the UM-WP and UN-WP samples was placed separately inside a muffle furnace according to

Fig. 1 a, **b** The UM-WP and UN-WP samples
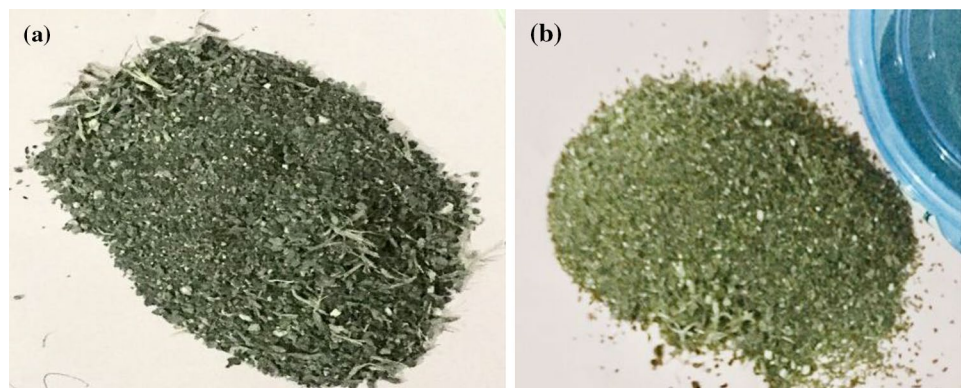
ASTM E775-78 standards using PerkinElmer 2400 Series II as described by [7]. The HHV was determined using the known elemental composition with Eq. (1), which is acceptable for engineering calculations:

$$HHV\ [MJ/kg] = 0.3491x\ (\%C) + 1.1783x\ (\%H)$$
$$- 0.1034x\ (\%O) + 0.1005x\ (\%S)$$
$$- 0.0151x\ (\%N) - 0.0211x\ (\%Ash) \quad (1)$$

Thermogravimetric analysis (TGA)

The thermal analysis was to determine the change in the sample mass under certain conditions of temperature, time and atmosphere. These analyses were carried out on UM-WP and UN-WP biomass samples with a TGA thermostep analyzer manufactured by ELTRA, Germany. 5 mg and 10 mg portion of the samples were prepared and heated from ambient temperature to 1000 °C at 10 °C min^{-1} under N_2 as described by [7]. The weight loss, fixed carbon, ash content, moisture, and heating rate were monitored and recorded.

SEM and EDXS analysis

The change in micrographs of the UM-WP and UN-WP samples was examined under SEM (VEGA 3 TESCAN-LMH). In this experiment, the sample was coated with a thin layer of carbon as a non-conducting adhesive at 50/60 Hz, 230 V and 1300 VA.

Elemental compositions of the UM-WP and UN-WP samples were analyzed using energy-dispersive X-ray. In this experiment, the energy is dispersed to determine the individual elements and to point out the lateral variation of its composition from chosen areas.

Results and discussions

Proximate analysis

As observed in Figs. 2 and 3 and Table 1, the compositions of UM-WP and UN-WP found are slightly different from the pretreated biomass. This happens due to the pretreatment technique and the composition of the original biomass. For proximate analysis, the thermal degradation of UM-WP and UN-WP in an inert atmosphere at different rates of heating showed a peak temperature of 35–108 °C which corresponds to the moisture loss with percentage content of 13.125 wt% and 13.011 wt%. The second peak was observed between 105 and 915 °C as shown in the TG-DTG curves, which is associated with VM content with a mass loss of 69.901 wt% and 69.723 wt%. The high VM found in the UM-WP suggests the high potential of this residue for energy production by pyrolysis [12].

The significant amount of FC for UM-WP and UN-WP was found to be 11.017 wt% and 11.278 wt% which corresponds to 715–750 °C, respectively. The ash content was found to be low at 5.957 wt% and 5.988 wt%, respectively. As previously presented, any biomass with an ash content

Fig. 2 TG-DTG curve of UM-WP
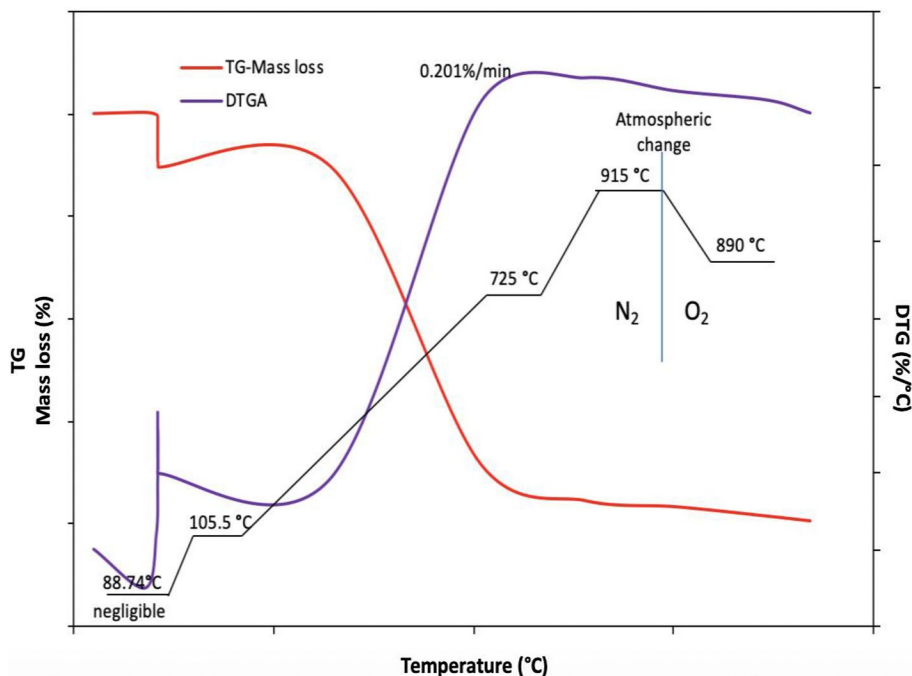
Fig. 3 TG-DTG curve of
UN-WP
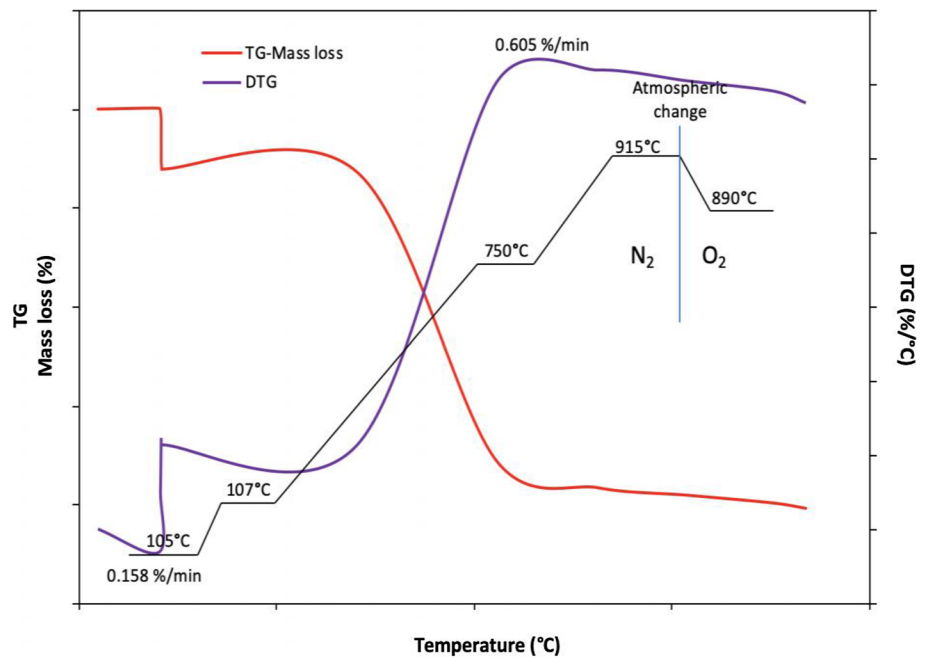
Table 1 Fuel composition of UM-WP and UN-WP biomass

Samples	Particle size (mm)	Proximate analysis				Ultimate analysis					HHV* (MJ/kg)
		MC	VM	Ash	FC	C	H	N	O	S	
		(wt. %) on db				(wt. %)					
UM-WP	0.7	13.125	69.901	5.957	11.017	45.95	4.26	1.13	48.02	0.64	15.52
UN-WP		13.011	69.723	5.988	11.278	43.49	4.51	3.16	47.91	0.93	15.49

[a]Calculated HHV (MJ/kg)

db dry basis

less than 5–6% does not undergo knocking trends [7, 13, 14]. The temperature range of thermal degradation of untreated waste peel is wider than that for pretreated waste peel. This trend is due to thermal stability and requires a longer retention time during the pyrolysis process. A residual mass of ~ 18% was observed from the samples that did not thermally degrade even at 1000 °C as similarly observed by [7, 11].

Ultimate analysis

As shown in Table 1 (ultimate analysis), the C, H, and O contents of UM-WP were found to be 45.95 wt%, 4.26 wt%, and 48.02 wt%, respectively; while the UN-WP was found to be 43.49 wt%, 4.51 wt%, and 47.91 wt%, respectively. The UM-WP has higher oxygen content which indicates a higher thermal reactivity than char [15]. This is essential because the more the oxygen content in a fuel, the easier it is to ignite [7, 16]. The decrease in O and H content in

biomass fuels can be associated with the scission of weak bonds within the char structure [7]. These resources (UM-WP and UN-WP) might be environmentally friendly with a certain amount of S (0.64 wt% and 0.93 wt%, respectively) and N (1.13 wt% and 3.16 wt%, respectively). The HHVs were found to be 15.52 MJ-kg^{-1} and 15.49 MJ-kg^{-1}, respectively, which might be high enough for consideration as a source of energy. However, the ignition of such high volatile fuels may lead to high flame length unlike low volatile fuels which ignite less readily [7]. The higher the volatile content in a fuel, the higher the HHV and the less heat is required for the thermochemical reactions [7, 17].

Thermal analysis

The thermal pyrolysis behavior obtained reveals the three different regions at elevated temperatures, which is related to elimination of hemicellulose (100–250 °C), cellulose (350–520 °C), and lignin (500–640 °C). The maximum mass

loss rate was about 0.201% min^{-1}, which corresponds to a peak temperature of about 639.46 °C in UM-WP. The maximum mass loss rate was about 0.605% min^{-1}, which corresponds to a peak temperature of about 770.8 °C in UN-WP (see Figs. 2 and 3).

The TG-DTG curves showed the presence of endothermic peaks with corresponding temperatures of 88.74 °C and 105 °C. These show that the endothermic peaks obtained refer to the onset of combustion, which is associated with the presence of hydrated or adsorbed water [18]. The UM-WP showed an obvious decrease during the exothermic reaction, confirming the presence of a few organic compounds which were exothermic.
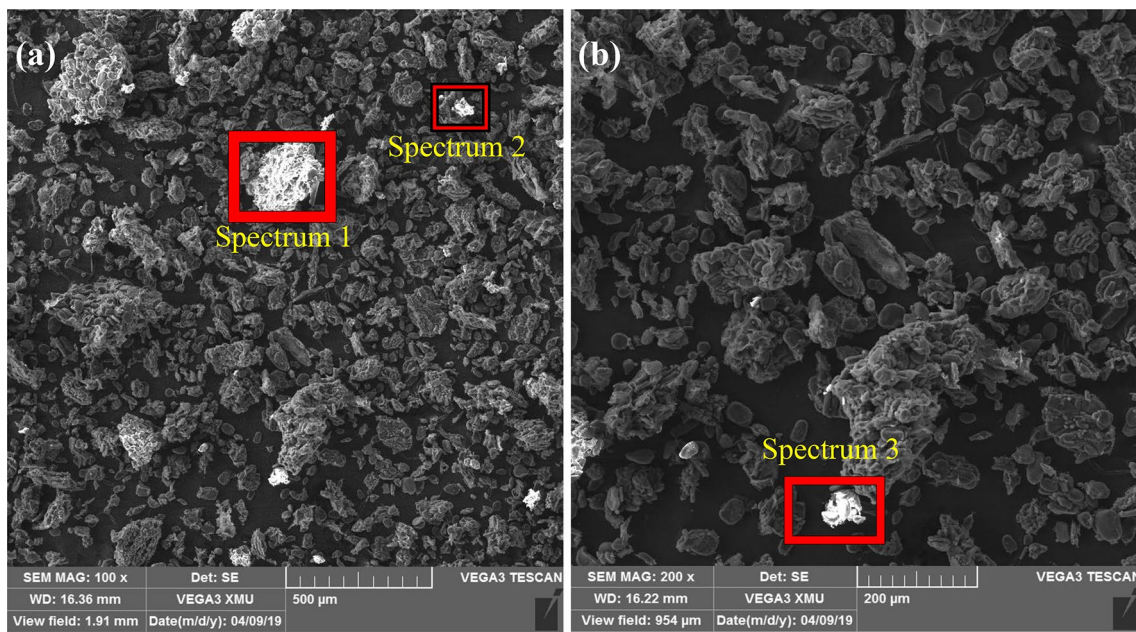
Fig. 4 **a**, **b** SEM images of UM-WP at 100× and 200×, respectively
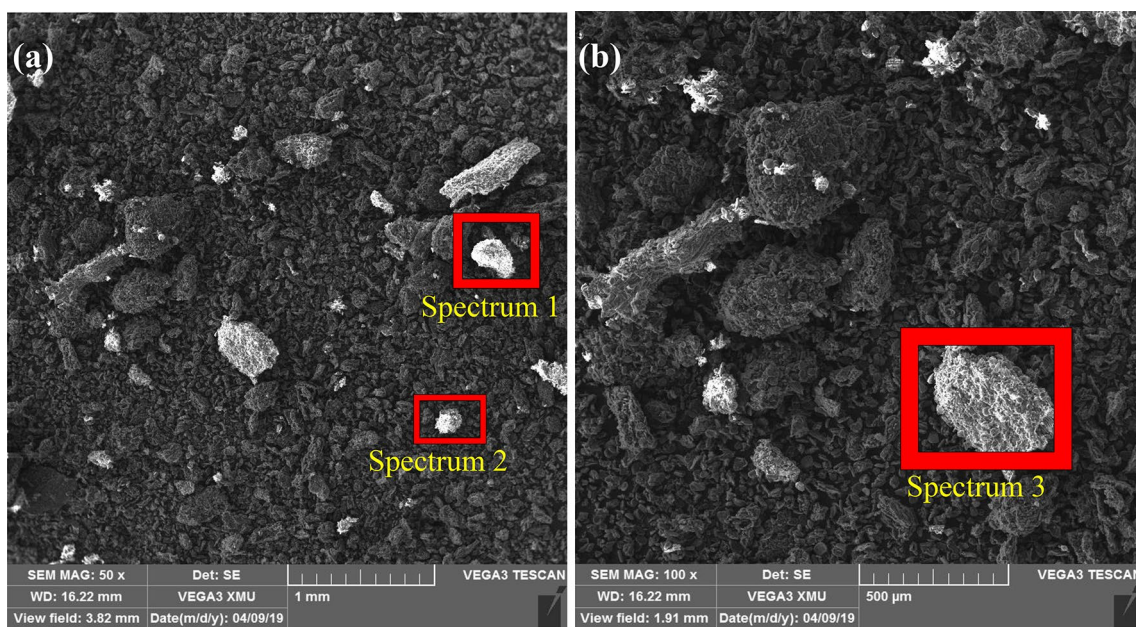
Fig. 5 **a**, **b** SEM images of UN-WP at 100× and 400×, respectively

SEM analysis of UM-WP and UN-WP

Figures 4a, b and 5a, b show the results of the morphological analysis of the UM-WP and UN-WP samples using SEM (sieved fraction of 200 μm, 500 μm and l mm). The morphologies of the samples were very similar. The micrographs revealed that the UM-WP and UN-WP have large and irregular particles and starch granules with high cellulose content, which are due to the increases in restrictions on molecular motion [19, 20]. These results might cause the oxygen to easily disperse inside the particles during combustion because the combustion reactivity of a biomass directly relates to the char morphology formed [7]. During carbonization of UM-WP and UN-WP, high fluidity and bubbles were produced due to the release of a large amount of volatile matter and which form a porous structure, which flows through the fluid mass and produces a non-homogeneous vacuolated structure [21, 22].

EDXS analysis of UM-WP and UN-WP

In the study, the EDXS was used to determine the elemental composition and to provide a structural idea of the biomass sample as illustrated in Figs. 6a–c and 7a–c. White spots appear in the sample which are elements. White spots are observed during SEM which was indicated in the form of spectrums as illustrated in Figs. 4a, b and 5a, b. These are elements from different categories as analyzed using EDXS.

The elements identified were potassium (K), magnesium (Mg), phosphorus (P), oxygen (O), carbon (C), nitrogen (N), sulfur (S), chlorine (Cl), silicon (Si), and cobalt (Co) (as
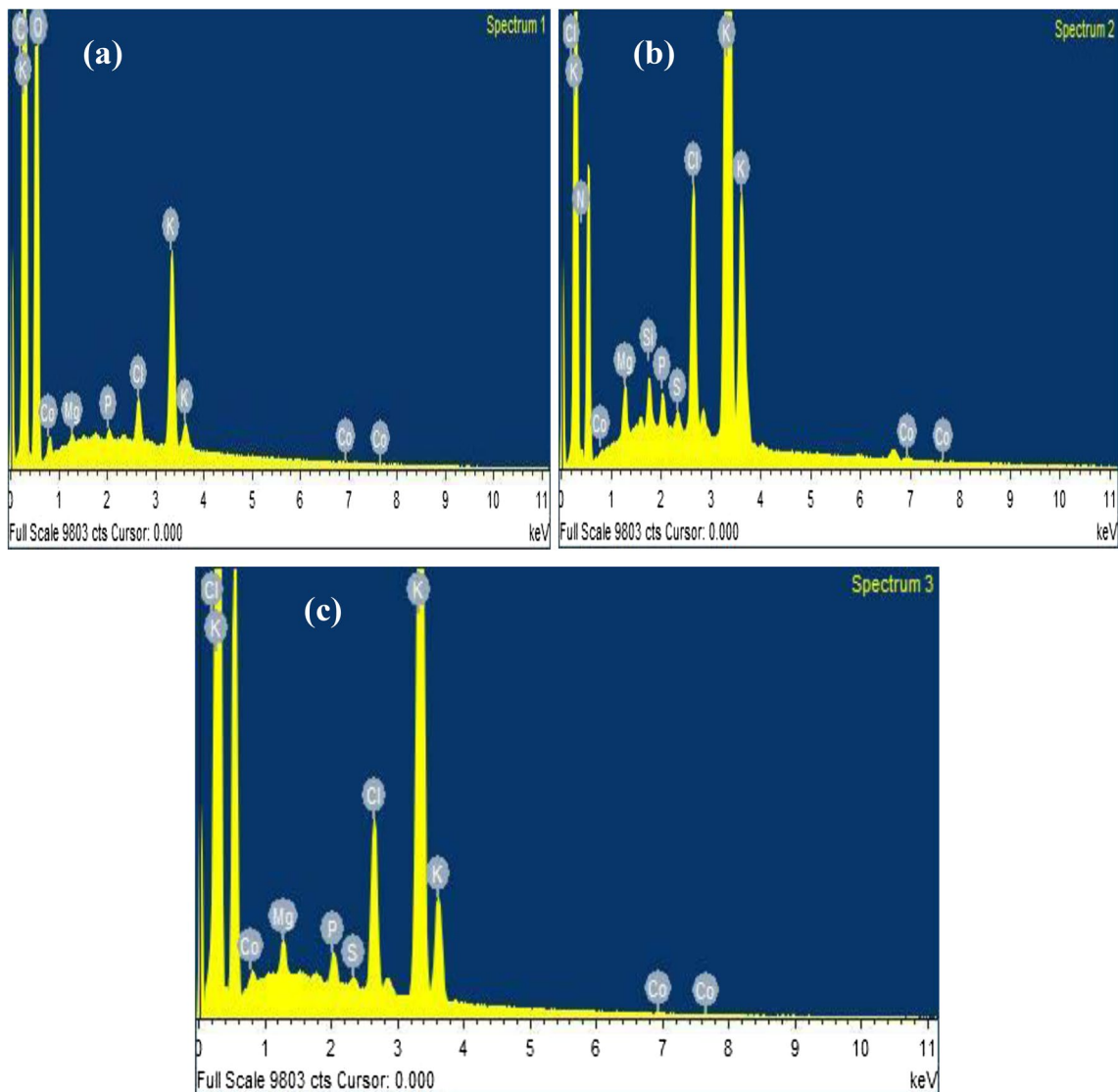
Fig. 6 **a**, **b**, and **c** EDXS spectrums of UM-WP at different points
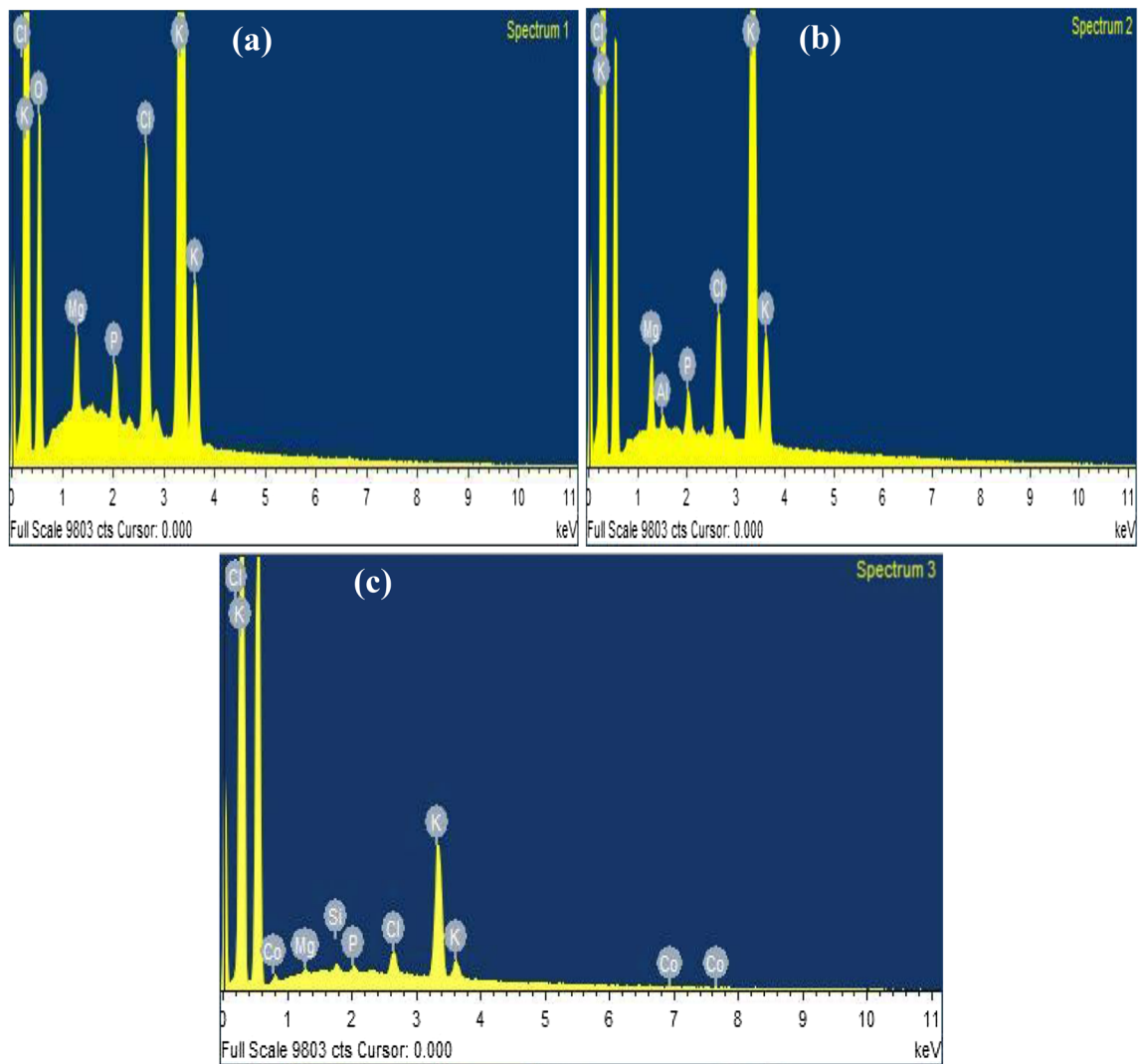
Fig. 7 **a**, **b**, and **c** EDXS spectrums of UN-WP at different points

shown in Table 2). Among these, the percentage of Mg, K and P decreased with an increase in C and O after pretreatment [7]. Besides, the percentage of O was found to be less compared to that of C. This trend is due to the fact that carbon forms the structural unit of cellulose and hemicelluloses. During combustion of biomass, the final solid phase is the most essential stage to the problem of alkali metals. The elements such as Cl, Si, S, Mg facilitates the mobility of several chemical species, particularly K, O and Fe, which is confirmed by KCl in deposits adherent [23], SiO_2, FeS_2, MgO, shows in Table 2 elemental compositions of UM-WP and UN-WP using EDXS. This biomass might grow an interest in the preparation of SiO_2, FeS_2, and MgO particles for a variety of applications, where the purity of materials is one of the most essential key parameters. Pure SiO_2 particles with crystalline phase can be used as the material source in photovoltaic [24], humidity sensors, film substrates and

ceramics [25]. Pyrite (FeS_2) is a promising photoelectric material for solar energy conversion and storage [26].

Conclusion

This research presents new biomass accessible in Uganda for future bioenergy production. The HHV was found to be 15.52 MJ-kg^{-1} and 15.49 MJ-kg^{-1} for UM-WP and UN-WP, respectively. As compared to pretreated biomass, it was found that the smaller particle sizes had only minor intra-particle gradients and the bigger particle sizes had more of a linear pattern variation. The micrographs showed irregular particles and starch granules with high cellulose content which might enable the oxygen inside the particles to disperse more easily during combustion. The amount of O was found to be less compared to C in

Table 2 Elemental compositions of UM-WP and UN-WP as analyzed using EDXS

Sample	Element	Elemental compositions (wt. %)		
		Spectrum 1	Spectrum 2	Spectrum 3
UM-WP	C	17.17	*	*
	O	16.38	*	*
	K	61.01	65.87	80.08
	N	*	23.36	*
	Cl	4.29	6.65	13.73
	Mg	2.49	1.23	2.54
	P	3.07	0.89	2.43
	Si	*	1.01	*
	S	*	0.43	0.88
	Co	-0.41	0.57	0.34
UN-WP	C	*	*	*
	O	49.34	*	*
	K	39.94	81.22	81.09
	N	*	*	*
	Cl	7.33	9.58	10.43
	Mg	1.98	5.40	2.34
	P	1.41	3.14	*
	Si	*		2.52
	Al	*	0.65	*
	Co	*		0.92

*Not detected

UM-WP. This trend is due to the fact that carbon forms the structural unit of cellulose and hemicelluloses. It is suggested that this exploration shows that UM-WP and UN-WP can be added to the biomass database as alternative energy sources, and material source for photovoltaic.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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Chapter 7: Paper 6

Bioethanol production from different *Matooke* peels species: A surprising source for alternative fuel

This chapter investigates the feasibility of producing bioethanol fuel from a renewable and sustainable energy resource which is *matooke* species peels through a fermentation process using *Saccharomyces cerevisiae*. The properties of the bioethanol were measured according to relevant ASTM standards and compared and analyzed by gas chromatography. These bioethanol properties are within the acceptable range of standard ethanol and gasoline. The article has been published in the *Case Studies in Thermal Engineering*, ELSEVIER BV.

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Bioethanol production from different *Matooke* peels species: A surprising source for alternative fuel

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ABSTRACT

Conversion of agro-industrial wastes to energy is an innovative technique for waste valorization and management which reduces exhaust emissions and offers socioeconomic benefits. The goal of this paper is to investigate the feasibility of producing bioethanol from a renewable and sustainable energy resource which is *matooke* species peels through a fermentation process using *Saccharomyces cerevisiae*. The properties of the bioethanol were measured according to relevant ASTM standards and compared, and analyzed by gas chromatography. The results shows that the bioethanol yield for the two samples through fermentation process was found to be 71.54 g/L for the *Mbwazirume* variety and 70.57 g/L for the *Nakyinyika* variety, and the selected parameters have a strong correlation with the ethanol yield, as analyzed by ANOVA. In conclusion, *matooke* bioethanol properties are within the acceptable range of standard ethanol and gasoline. These *matooke* bioethanol can be used in the development of further experiments on performance and exhaust emissions test in spark-ignition (SI) engines.

1. Introduction

Dependency on other countries for fuel and the negative influence that modern-day fuels have on environmental issues such as global warming and environmental pollution [1] have led to the investigation of environmentally friendly, renewable and sustainable energy fuels such as biofuels. Among the biofuels, bioethanol has been identified as the most used alternative fuel worldwide due to its significant contributions to a reduction in crude oil consumption, high oxygen content, high octane number, non-toxicity and reduced emission characteristics compared to gasoline, thus promoting a cleaner environment for the future [2–5]. Bioethanol can be produced from various types of agro-industrial residue or renewable sources through a fermentation process using microorganisms such as yeast. Most of the agro-industrial residues, such as banana peels, represent about 40% of raw processed fruit [6]. Banana peel, also known as banana skin, is the outer covering of the banana fruit. Banana is one of the most consumed fruits in the world. Uganda is among the largest producers of bananas, with an annual per capita consumption of 240 kg [7]. There are different types of bananas grown in Uganda for food consumption. These have been classified as green cooking bananas (*matooke*), plantain, and sweet bananas [8,9].

Matooke is a variety of banana indigenous to South West Uganda. It comes from the family of bananas known as the East African highland bananas. *Matooke* cannot be peeled in the same way as ordinary (sweet) bananas due to the high starch content. They appear to be green in color and thick at the midsection [10]. Once the peel is removed, the fruit cannot be eaten raw but can be cooked, and the peels are generally discarded or used as feedstock for cattle, goats, and pigs. However, there are some concerns about

their utilization, including poor storage ability and heavy contamination due to indiscriminate dumping. The average storage length of market crop wastes for matooke peels is 1–3 days [11]. Nevertheless, these wastes can be utilized as a readily available and renewable low-cost raw material for bioethanol production due to the high starch content.

Research has been conducted on the acid hydrolysis of starch to glucose, but little research has been done till now using banana peel as a substrate for fuel production [12]. Generally, starch-based biomass depends on the feedstock and the steps involved in the bioethanol production process [13]. Therefore, bioethanol production consists of various steps, namely, pre-treatment, hydrolysis, fermentation, distillation, and dehydration [14–16]. Many studies have reported that bioethanol fuel has more oxygen molecules which contribute to faster flame speed, leading to enhanced combustion initiation and stability, avoids knocking, has a good cold start, and improves efficiency for spark-ignition (SI) engines [17–22].

This research aimed to use different green cooking bananas (matooke) peels such as Mbwazirume and Nakyinyika for bioethanol production as an alternative fuel for SI engines since it is lignocellulosic biomass and matooke peels do not compete with food crops. The purpose of selecting various species is to study which matooke peels produce the highest bioethanol in volume and concentration by conducting GC – FID/MS tests, also optimized using (ANOVA).

2. Material and methods

2.1. Material

2.1.1. Raw materials

The raw material for this research was limited to two specific species of matooke, namely, sample A (Mbwazirume) and sample B (Nakyinyika). These matooke species were obtained from different locations in Uganda. The study recorded about 38.57% of the weight waste peels per fruit.

2.1.2. Experimental apparatus and solvents

The experimental apparatus and solvents used were: grant OLS 200 shaking water bath, Sox-Tec extractor, furnace, rotary evaporator, digital pH meter (ASTM D7946), electric grander. Sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), sodium sulphate anhydrous ($NaSO_4$), baker's yeast (Saccharomyces cerevisiae), automatic bomb calorimeter, GC-FID, GC-MS (Agilent Technologies
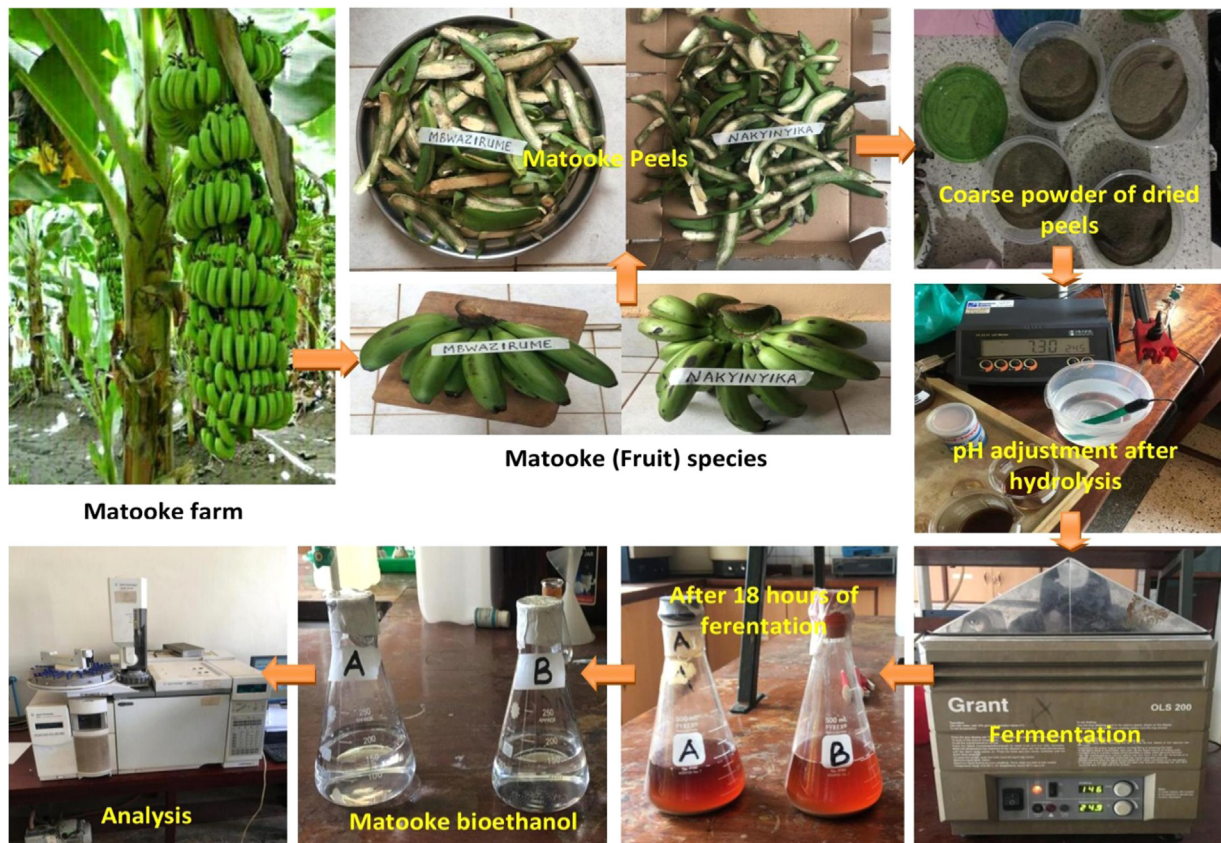
Fig. 1. Process steps leading to extraction of bioethanol from matooke peels.
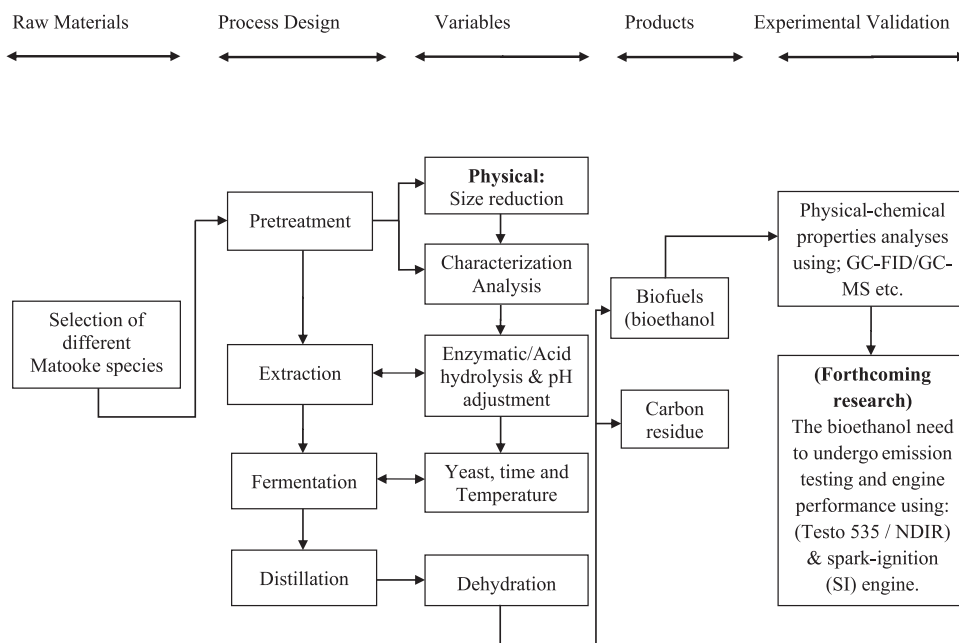
Fig. 2. Experimental layout of bioethanol development.

5975), lovis 2000 M/ME micro-viscometer, hydrometer, elemental analyzer (ASTM D5291), 250/500 ml beakers, 250/500 ml Pyrex Erlenmeyer flasks and distilled water. A schematic diagram of the experimental process is shown in Fig. 1.

2.2. Methods

2.2.1. Experimental overview

Fig. 2 shows the research design for the production of bioethanol from biomass such as *Mbwazirume and Nakyinyika* peels using various variables. Bioethanol production from biomass comprises different stages: pretreatment, hydrolysis of cellulose and hemi-cellulose, separation of lignin residue, sugar fermentation, and distillation and purification of the bioethanol to meet fuel specifications [23,24]. After testing the physical and chemical properties of bioethanol, these fuels can be used in the development of further experiments on performance and exhaust emissions test in an internal combustion engines.

2.2.2. Pretreatment

The purpose of the pretreatment process is to make the cellulose accessible to hydrolysis for conversion to fuels. Various pre-treatment techniques change the physical and chemical structure of the lignocellulosic biomass and improve hydrolysis rates [25]. In this study, the peels were separated from the fruit and washed with distilled water. The two hybrids of *Matooke* peels were shade dried for 83 h. The size of the materials is 10-30 mm after chipping and 0.2-2 mm after milling, and grinding with electrical grinder to make a coarse powder and stored in different containers at room temperature till further analysis. The energy requirements dependent on the final particle size and reduction in crystallinity of the lignocellulosic material.

2.2.3. Proximate analysis

Proximate analysis is the determination of the major components within the raw material (*Matooke* peels), which include: moisture content, ash, crude fats, protein, dietary fiber, and carbohydrates. In this analysis, compositions are determined using the below standard methods in Table 1. The proximate analysis was carried out at the School of Food Technology, Nutrition, and Bio-Engineering, Makerere University Kampala, Uganda.

Table 1
List of standard method used in proximate analysis.

Test name	Standard method
Moisture content	ASTM D2216-98
Volatile content	BS3797
Ash content	ASTM D2974

2.2.4. Hydrolysis

50 g of each variety of dried peels powder were transferred into two labeled conical flasks (A & B) and 150 ml of 0.5% (v/v) to 2.5% (v/v) diluted sulfuric acid (H_2SO_4) was added to each. The flasks were covered with a tapered cork to avoid the entrance of water or loss of liquid due to evaporation. The two flasks were placed in a shaking water bath for about 50–90 °C $\pm$ 1 °C at 20–60 min with gentle shaking for homogeneity of mixture solution. After hydrolysis, the two samples were allowed to cool to room temperature before the filtration process was carried out. The insoluble particles were separated from the hydrolysate using filter paper.

2.2.5. Fermentation

Fermentation is the process of converting the pentose and hexose into ethanol using microorganisms, such as bacteria, yeast, or fungi. Fermentation of lignocellulosic hydrolyzates is challenging but depends on the method and microorganisms used. A microorganism such as yeast serves as a key factor in fermentation and has an important role in meeting those challenges. The two samples were prepared for the fermentation process, and pH adjustment was carried out with 1 M NaOH until the pH reached 5.0, because when the pH was above 5.0, the concentration of ethanol reduced substantially [26]. This process was carried out in 500 ml Pyrex flasks. Each flask containing hydrolyzed sample mixed with 6.5 g to 8.5 g of *Saccharomyces cerevisiae* (yeast). The solutions were sealed and manually shaken for proper mixing, and then placed in a shaker water bath at 29–39 °C $\pm$ 1 °C at 165 rpm for about 10 h to 30 h for the fermentation process. After shaking, the mixtures were withdrawn and kept for 18 h to allow the particles from the liquid to settle. The three variables were time, temperature and yeast content; and 17 runs per sample were conducted to produce ethanol after fermentation and optimized using the response surface method (RSM).

2.2.6. Distillation

Bioethanol extraction was carried out through the process of distillation and dehydration. Distillation was carried out using a rotary evaporator at temperature, pressure and the rotary speed of 55 °C $\pm$ 1 °C, 175 mbar, and 70 rpm, respectively. Dehydration was done by using sodium sulphate anhydrous ($NaSO_4$) for eliminating the water molecules within the bioethanol.

2.2.7. GC analysis

In this method, the GC-MS was used to identify the molecular weights and structures that are within the two different samples of *matooke* peels. This analysis was conducted at Chemiphar Uganda limited and Makerere University Kampala, Uganda. The injector temperature was at 250 °C. The initial oven temperature was programmed for 80 °C (hold for 2 min) increased to 120 °C at a rate of 5 °C/min (and hold for 2 min) then increased to 240 °C at a rate of 10 °C/min (hold for a few moments), and finally increased to 420 °C at a rate of 15 °C/min (hold for a few minutes).

The second analysis was conducted using GC-FID with automatic injection along with a blank consisting of demineralized water and standard solutions to measure the ethanol content within the samples and then compared with the initial analysis. The blank was injected first followed by the standard solutions. The samples were injected according to presumed alcohol content, with the samples containing least amount of alcohol injected first. This was to prevent carry-over from high concentrated alcohol samples to those with low alcohol content. Every standard solution and sample was injected in duplicates. The inlet was set at a temperature of 225 °C with splitless injection, and the injection volume was 1 μL. The column used was a Phenomenex ZB-FFAP GC-column, which is a high polarity column that is 30 m $\times$ 320 μm $\times$ 0.25 μm.

The oven was set at a programme that had an initial temperature of 50 °C (held for 2 min) the increased to 245 °C at a rate of 45 °C per minute and held at 245 °C for 1 min. The flame ionization detector temperature was set at 285 °C with a flow of 30 ml/min H2, and the flow rate of O2 was set at 300 ml/min. Finally, the total run was 24 min long, and the injection syringe was rinsed with demineralized water between every injection.

2.2.8. Fuel properties of bioethanol

The fuel properties of bioethanol produced from *matooke* peels were tested according to the ASTM standard methods. The fuel properties of bioethanol from different *matooke* species' peels were determined experimentally to ascertain their suitability as an alternative fuel and compared with ethanol ASTM D4806 and gasoline. The equipment used to analyze the properties and chemical properties of the bioethanol are summarized in Table 2.

Table 2
List of equipment used to analyze the properties of the *Matooke* bioethanol.

Property	Equipment	Standard method
Kinematic viscosity	Lovis 2000 M/ME micro viscometer	DIN 53,015
Density	Micro density meter (Anton Paar)	ISO 12,058
Elemental analysis for carbon (C), hydrogen (H) and oxygen (O)	CE-440 CHN Elemental Analyzer (EIA)	ASTM D5291
Calorific value	IKA C2000 basic, automatic bomb calorimeter	ASTM D240
Ethanol content	Gas chromatograph, Agilent 7890 A	ASTM D4806
Flash point	Flash point tester	ASTM D93

Table 3
Proximate Composition of *Matooke* Peels.

Parameter measured	Units	Sample result	
		A	B
Moisture content	(g/100 g)	8.51	8.71
Ash content	(g/100 g)	8.23	7.74
Crude protein	(g/100 g)	5.53	4.84
Crude fat	(g/100 g)	3.99	3.13
Dietary fiber	(g/100 g)	14.10	10.92
Carbohydrates	(g/100 g)	72.23	72.85

3. Results and discussion

3.1. Proximate composition of matooke peels

The proximate compositions of the *matooke* peel samples were found to be high in carbohydrate content, especially *Nakyinyika* (sample B) with 72.85%, and a significant amount of moisture, ash, protein, fat, and fiber content. The results of the proximate composition are shown in Table 3. The presence of more than 70% of carbohydrates in these samples makes it a potential substrate for bioethanol production.

3.2. Analysis of reducing sugar

The reducing sugar content in the hydrolysate (filtrate) was analyzed using 3,5-dinitrosalicylic acid (DNS) method [27]. In these results 1:1 of sample to DNS reagent is used: the analyze 5 ml of hydrolysate was mixed with 5 ml of DNS reagent heating in a thermocycler (100 °C, for 3 min). The reaction mixture was cooled to room temperature and quantifies at 575 nm, then the most appropriate wavelength was selected based on sample absorbance. The amounts of (0–100 g/L) reducing sugars were measured for each sample using ultraviolet-visible spectrophotometer. However, various effects were considered such as pH at 5.0, temperature at 50, 70 and 90 °C, time of 20, 40 and 60 min, acid concentration of 0.5%, 1.5% and 2.5% (v/v) as shown in Table 4.

3.3. Experimental results of bioethanol and optimization conditions

After determining the optimal conditions for fermentation, the results were evaluated using Design-Expert® version 11. The effects of the controlled variables, such as yeast, time and temperature, were investigated using ANOVA and Box-Behnken design. All experiments were run in a random order. The optimal conditions were then calculated by the regression model and consequently verified experimentally. Table 5 shows the experimental and Box-Behnken design, and 17 runs were conducted to produce ethanol contents from sample A and B. The experimental and predicted outputs of the ethanol content shows closeness in sample A, which indicates that the Box-Behnken design was successful and the results are optimal. However, for sample B, both outputs differed slightly.

The analysis of variance (ANOVA) was carried out to determine the statistical significance of the quadratic response surface model as tabulated in Tables 6(a) and 6(b) for the two samples (A and B), respectively. Table 6(a) and 6(b) show the analysis of variance for P-values, where a P-value of less than 0.0500 indicates that the model terms are significant. In this case Z, XY, YZ, X^2, Y^2, Z^2 and Z, XZ, Y^2 are quite significant influences on ethanol content. Values greater than 0.1000 indicate the model terms are not significant.

The result shows that the coefficient of determination (R^2) in Table 6(a) and 6(b) was found to be 0.9872 and 0.8622, which indicates that 98.72% and 86.22% of the experimental data were relevant and the model did not explain 1.28% and 13.78% of the total variations. Therefore, the Lack of Fit F-value of 13.79 and 356.55 implies the models are significant. In Table 6(a), the predicted coefficient of determination (R_p^2) was found to be 0.8110 which is in reasonable agreement with the adjusted coefficient of determination (R_a^2) of 0.9707; the difference is less than 0.2. This shows that the (R_a^2) was found to be very high, which implies that the model accounted for 97.07% of the variability in the data. However, Table 6(b) shows different trends with a contrary predicted (R_p^2)

Table 4
Experiment of reducing sugar content in *matooke* species peels.

Matooke species peels	Acid concentration % (v/v)	Temperature (°C)	Time (min)	Reducing sugar (g/L)
Mbwazirume (A)	0.5	50	20	76.83
	1.5	70	40	77.03
	2.5	90	60	75.96
Nakyinyika (B)	0.5	50	20	74.55
	1.5	70	40	75.32
	2.5	90	60	75.07

Table 5
Experimental and Box-Behnken predicted results of ethanol contents.

Experiment run	Yeast (g)		Temperature (°C)		Time (hr)		Experimental		Predicted output	
							Ethanol content (%v/v)			
	A	B	A	B	A	B	A	B	A	B
1	6.5	6.5	29	29	20	20	86.42	88.66	86.04	85.39
2	7.5	7.5	40	40	10	10	85.9	88.03	85.87	87.26
3	7.5	7.5	34.5	34.5	20	20	90.2	92.36	90.1	92.24
4	8.5	8.5	34.5	34.5	10	10	84.8	86.94	84.45	92.24
5	7.5	7.5	34.5	34.5	20	20	90.3	92.4	90.1	91.68
6	8.5	8.5	34.5	34.5	30	30	87.12	89.26	86.84	91.14
7	7.5	7.5	34.5	34.5	20	20	90	92.14	90.1	90.09
8	6.5	6.5	40	40	20	20	88.54	90.68	88.3	92.24
9	6.5	6.5	34.5	34.5	10	10	84.4	86.51	84.68	88.96
10	8.5	8.5	29	29	20	20	88.02	90.14	88.27	92.24
11	7.5	7.5	34.5	34.5	20	20	90	92.14	90.1	89.08
12	7.5	7.5	34.5	34.5	20	20	90	92.14	90.1	86.73
13	7.5	7.5	29	29	10	10	84.4	86.53	84.5	96.02
14	7.5	7.5	40	40	30	30	86.8	88.95	86.7	92.24
15	8.5	8.5	40	40	20	20	85.96	88.1	86.34	86.81
16	6.5	6.5	34.5	34.5	30	30	86	98.16	86.35	89.14
17	7.5	7.5	29	29	30	30	87.7	89.84	87.73	89.5

Notes: A and B indicates the label of the samples (A-*Mbwazirume*; B-*Nakyinyika*).

Table 6a
Analysis of variance (ANOVA) results of the ethanol content for sample A.

Source	Sum of squares	df	Mean square	F-value	p-value	Remarks
Model	69.8	9	7.76	59.83	< 0.0001	significant
X-Yeast	0.0364	1	0.0364	0.2812	0.6123	–
Y-Temperature	0.0544	1	0.0544	0.42	0.5376	–
Z-Time	8.24	1	8.24	63.57	< 0.0001	–
XY	4.37	1	4.37	33.69	0.0007	–
XZ	0.1296	1	0.1296	0.9997	0.3507	–
YZ	1.44	1	1.44	11.11	0.0125	–
X^2	12.78	1	12.78	98.61	< 0.0001	–
Y^2	5.31	1	5.31	40.92	0.0004	–
Z^2	32.48	1	32.48	250.55	< 0.0001	–
Residual	0.9075	7	0.1296	–	–	–
Lack of Fit	0.8275	3	0.2758	13.79	0.0141	significant
Pure Error	0.08	4	0.02	–	–	–
Cor Total	70.71	16	–	–	–	–
R^2	0.9872	–	Adjusted R_a^2	0.9707	–	–
C.V.%	0.4118	–	–	–	–	–

of −1.1979, which indicates that the overall mean may be a better predictor for ethanol content than the current model.

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. The quadratic model for ethanol content was regressed by considering the significant variables and is shown in Eq. (1) and Eq. (2) for sample A and B, respectively.

$$\text{Ethanol content}(\%v/v) = +90.1 + 0.0675X + 0.0825Y + 1.01Z - 1.04XY + 0.81XZ - 0.6YZ - 1.74X^2 - 1.12Y^2 - 2.78Z^2 \qquad (1)$$

$$\text{Ethanol content}(\%v/v) = +92.24 - 1.2X + 0.0738Y + 2.28Z - 1.02XY - 2.33XZ - 0.5975YZ - 0.4805X^2 - 2.36Y^2 - 1.54Z^2 \qquad (2)$$

The predicted ethanol contents versus experimental values (actual) were analyzed and shown in Fig. 3(a) and (b). In Fig. 3(a) it can be observed that all the data points are within the proximity of the regression line, which indicates that there is good agreement between the predicted ethanol content and experimental values. Therefore, the model satisfies the assumptions of the analysis of variance (ANOVA) and the error distribution is approximately normal. However, in Fig. 3(b) the model was not too good compared to Fig. 3(a), because the lower the coefficient of determination (R^2) means the weaker the goodness of the fit model. It is observed that the error might occur from the hydrolysis treatment.

3.4. Effects of yeast and temperature

The effect of yeast and temperature on the yield of ethanol is shown in Fig. 4(a) and (b). The response in Fig. 4(a) showed that

Table 6b

Analysis of variance (ANOVA) results of the ethanol content for sample B.

Source	Sum of squares	df	Mean square	F-value	p-value	Remarks
Model	117.39	9	13.04	4.87	0.0244	significant
X-Yeast	11.45	1	11.45	4.27	0.0776	–
Y-Temperature	0.0435	1	0.0435	0.0162	0.9022	–
Z-Time	41.41	1	41.41	15.44	0.0057	–
XY	4.12	1	4.12	1.54	0.255	–
XZ	21.76	1	21.76	8.12	0.0247	–
YZ	1.43	1	1.43	0.5326	0.4892	–
X^2	0.9721	1	0.9721	0.3626	0.5661	–
Y^2	23.46	1	23.46	8.75	0.0212	–
Z^2	9.96	1	9.96	3.71	0.0953	–
Residual	18.77	7	2.68	–	–	–
Lack of Fit	18.7	3	6.23	356.55	< 0.0001	significant
Pure Error	0.0699	4	0.0175	–	–	–
Cor Total	136.16	16	–	–	–	–
R^2	0.8622	–	Adjusted R_a^2	0.6849	–	–
C.V.%	1.82	–	–	–	–	–

Notes: C.V = coefficient of variance.
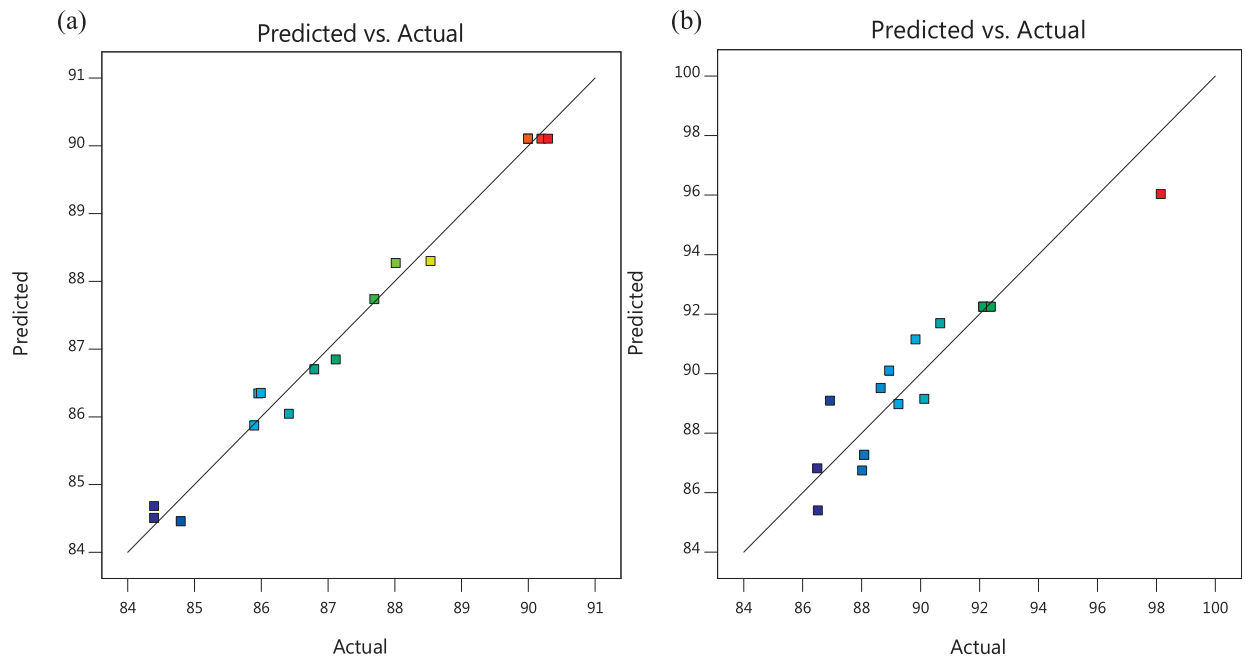
Fig. 3. Predicted output versus experimental (actual), (a) Sample A (b) Sample B.

when the level of yeast and temperature increased, the fermentation resulted in a high yield of ethanol and started decreasing when the temperature reached 35 °C with an increase in yeast, which implies that yeast and temperature are significant influences on ethanol content. This is due to the growth rate of the microorganisms (yeast), which is directly affected by the temperature [28]. The yield of ethanol increased with an increase in temperature but decreased in yeast content as shown in Fig. 4(b). This increase in ethanol yield is due to chemical reactions and other enzyme activity in the cells which are favored by temperature increases but to a certain level, and enzyme activity tends to be low at lower temperatures.

3.5. Effects of yeast and time

The effect of yeast and time on the yield of ethanol is shown in Fig. 5(a) and (b). The shaking speeds (165 rpm) were kept constant during the fermentation process. It was observed that there were no significant interactions between yeast and other variables affecting the results of ethanol. The graph shows some increment in yeast at a lower level of time (21.8 h), with an increase in the yield of ethanol (Fig. 5(a)). It was shown in Fig. 5(b) that with higher levels of yeast and time, the production of ethanol yield level decreased. This error may occur due to the effect of the hydrolysis treatment. However, the hydrolysis temperature increases at lower levels of acid concentration (versus versa) and might produce a positive or negative effect on the yield of ethanol. From the

(a)   (b)
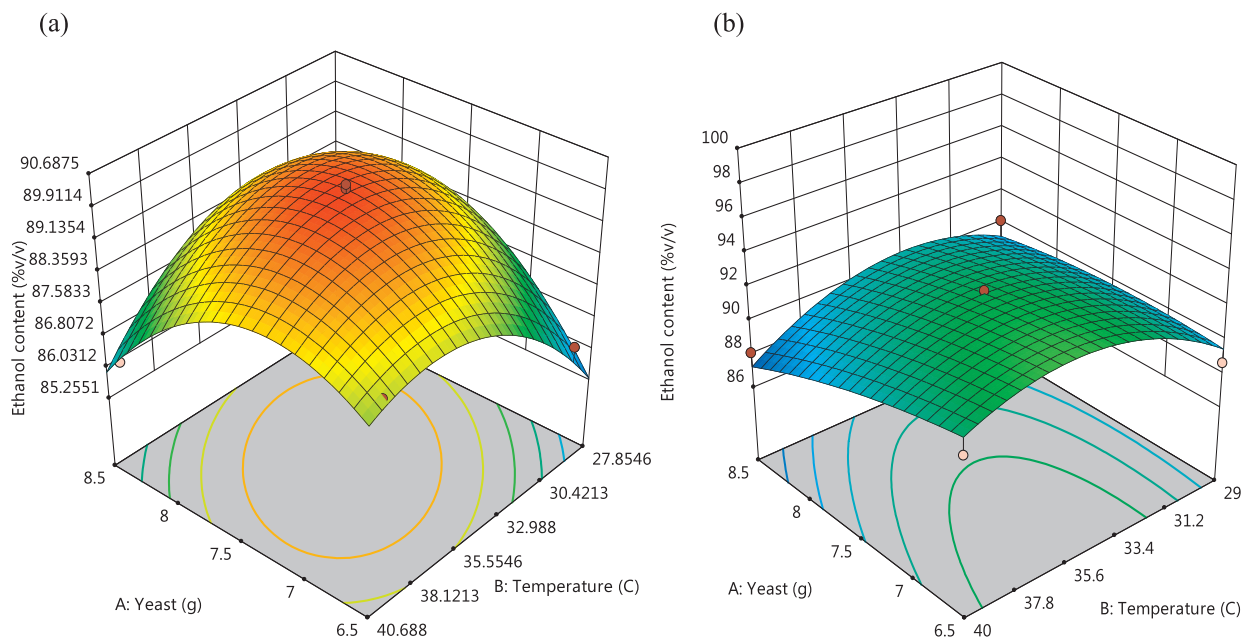
Fig. 4. Response surface plot of yeast and temperature on ethanol content when the time is fixed (20 h); (a) sample A (b) sample B.

(a)   (b)
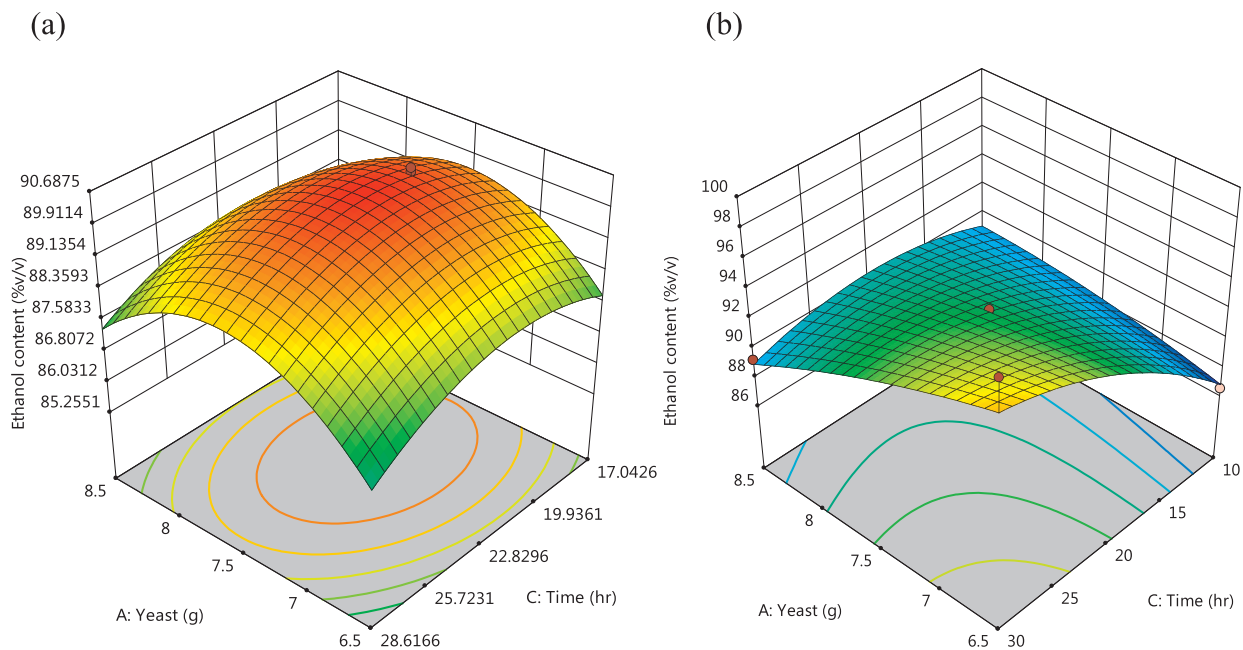
Fig. 5. Response surface plot of yeast and time on ethanol content when the temperature is fixed (34.5 °C); (a) sample A (b) sample B.

optimization, the optimum operating parameters for ethanol yield is 90.65%v/v and recorded at 33.39 °C temperature; 8.5 g yeast and 20.21 h time.

3.6. Effects of temperature and time

This study investigated the effect of reaction time and temperature on bioethanol conversion yield by varying the time range from 10–30 h and the temperature range from 29 °C to 40 °C when other variables were kept constant. Fig. 6(a) shows that conversion yield increases with increase in temperature. The maximum *matooke* bioethanol conversion yield is 90.19%v/v and recorded at 34.5 °C temperature and 21.833 h time. The yield at 33–35 °C is almost the same but decreases at 36 °C due to the evaporation temperature of the ethanol (Fig. 6(a)).

(a)   (b)
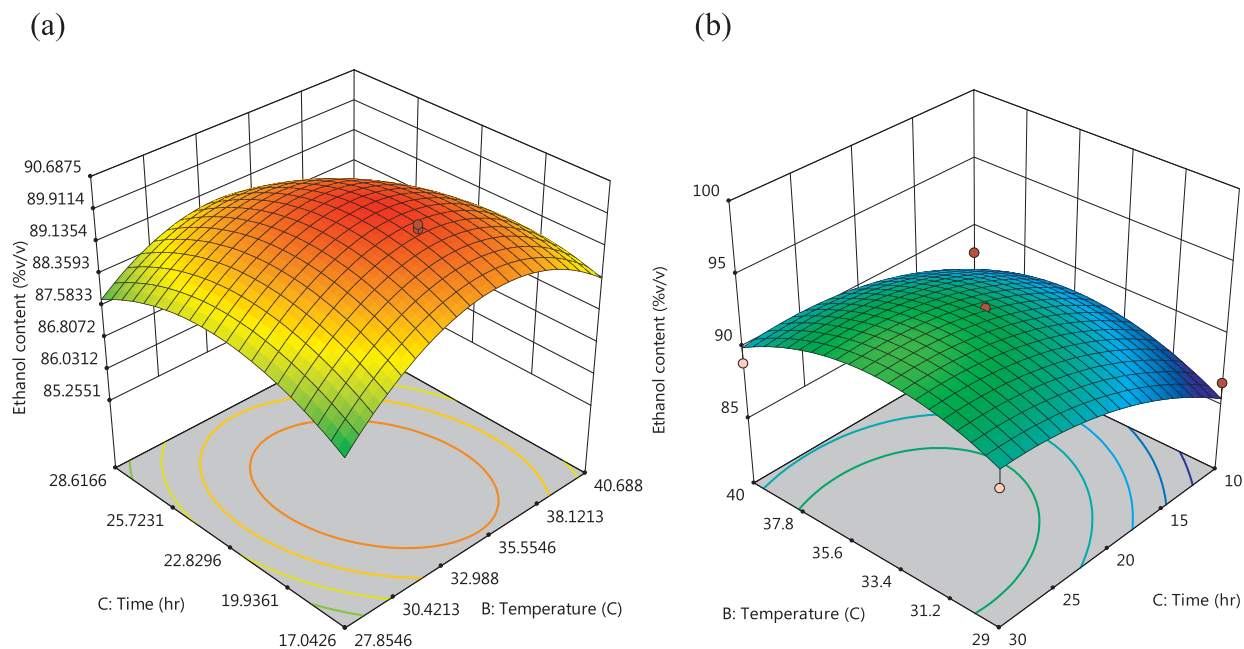
Fig. 6. Response surface plot of temperature and time on ethanol content when the yeast is fixed (7.5 g); (a) sample A (b) sample B.

Therefore, an increase in temperature and time had an insignificant effect on the ethanol yield, and it was evident that for fixed yeast, increasing the time would only increase ethanol production by a slight amount (Fig. 6(b)). A decrease in ethanol yield at a temperature above 36 °C is due to exceeding the optimal level and might eliminate the available oxygen or increase the toxic effect of ethanol in the medium due to dissociation of the molecules and also reduce enzyme activity due to denaturation of the enzymes giving no significant impact on ethanol yield.

3.7. Fuel properties of bioethanol from different matooke peels species

In this study, the fuel properties of the bioethanol from different *matooke* peels were determined, and each indicates the quality of fuel used for the spark-ignition engine. The physical and chemical properties of the *matooke* peel bioethanol are shown in Table 7. The density, heating values, ethanol content and viscosity of the fuels were measured using the ASTM standard. The study used an automatic bomb calorimeter (IKA C2000 basic) to measure the heating value of bioethanol using the ASTM D240 standard. The results show that the heating values of *matooke* bioethanol are slightly closer with the ethanol ASTM D4806. The measured fuels are within the acceptable range of standard ethanol and gasoline. However, these fuels can be used in the development of further experiments on performance and exhaust emissions test in an internal combustion engines.

4. Conclusion

In conclusion, this study evaluated two different agro-industrial wastes as the alternative potential for bioethanol production due to their low cost and easy availability in Uganda. The proximate result shows that the two different wastes (*matooke* peel samples) were found to be high in carbohydrate contents with 72.23% and 72.85% respectively, and only a little amount of other nutrients that could support microbial growth. Therefore, in sample A, the optimum operating parameters for ethanol yield is 90.19%, which were

Table 7
Comparison of fuel properties from different *matooke* peels bioethanol, ethanol, and gasoline.

Property	Units	Bioethanol *Mbwazirume*	Bioethanol *Nakyinyika*	Ethanol ASTM D4806 [16]	Gasoline [29]
Molecular formula	–	C_2H_5OH	C_2H_5OH	C_2H_5OH	C_4 -C_{12}
Composition (C, H, O)	Mass %	52, 13, 35	52, 13, 35	52.2, 13.1, 34.7	86, 14, 0
Density at 15 °C	Kg/m^3	793.2	778.5	785–809.9	737
Lower heating value	MJ/kg	26.3	26.1	26.9	43.5
Higher heating value	MJ/kg	29.1	28	29.7	47.3
Viscosity at 20 °C	mm^2/s	1.3	1.2	1.19	0.37 to 0.44
Flash point	°C	21.7	21.2	12–20	−45 to −13
Ethanol content	%vol.	90.19	90.65	99.9	–

Notes: Sample A – *Mbwazirume*; Sample B – *Nakyinyika*.

recorded at 34.5 °C temperature, 7.53 g yeast and 21.83 h time, which yielded 77.03 g/L reducing sugar. The maximum ethanol yield obtained in sample B is 90.65% recorded at 33.39 °C temperature, 8.5 g yeast and 20.21 h time, which yielded 75.32 g/L reducing sugar. These *matooke* bioethanol can be used in the development of further experiments on performance and exhaust emissions test in an internal combustion engines. Utilizing this waste biomass for bioethanol production through a biotechnological process not only helps to reduce environmental pollution but also reduce the dependence on oil-producing countries and supports rural economies by creating jobs and providing an additional source of income.

Acknowledgments

Conflict of interest

There was no potential conflict of interest on this research.

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Chapter 8: Paper 7

Effect of low bioethanol fraction on emissions, performance and combustion behavior in a modernized electronic fuel injection engine

This chapter examines the effects of low content rates of *Mbwazirume* bioethanol-gasoline blends (E0, E5, E10, and E15) in a modernized TD201 four-stroke petrol engine, equipped with efficient electronic fuel injection (EFI) systems. These blend fuels were tested under various engine speeds in order to assess engine emissions, performance, and combustion characteristics because ignition timing is also an alternative process to predict engine performance. The article has been published in the *Biomass Conversion and Biorefinery*, **SPRINGER Nature**.

ORIGINAL ARTICLE

Effect of low bioethanol fraction on emissions, performance, and combustion behavior in a modernized electronic fuel injection engine

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Abstract

This study examined the effects of low content rates of *Mbwazirume* bioethanol blends (5%, 10%, and 15%) with gasoline in a modernized electronic fuel injection (EFI) engine. The results showed that the E15 fuel ratio induced an increase in combustion duration with minimum premixing combustion duration, hence exhibited low emissions, high indicated power, and efficiency with low fuel consumption (at 12 to 18° CA aTDC). These results are due to the low content of carbon in bioethanol, which eliminates the occurrence of soot formation and requires less air to burn fuel blends with low luminosity and radiation. In E10 and E15 fuel, when the engine operated at 2700 rpm, the engine emissions were relatively low with a slight increase in performance, except for E5. The rate of NO_X formation rose higher with E5 and E10; this was due to the combustion advanced which led to higher temperature and in-cylinder pressure than that of E0 and E15. However, when the exhaust gas temperature (T_{eg}) was at 192 °C for 21.7 s fuel drain time (F_{dt}), the CO and CO_2 emissions decreased with E15 and increased rapidly with E5 and E10. In addition, the HC emissions decrease at all injection timings for E5, E10, and E15, except that of 10° CA bTDC which did not follow this trend. When the combustion phases are the same, the model results suggest that a little modification in the heat-transfer parameter has a great impact on the thermal efficiency.

Keywords *Matooke* bioethanol · Emissions · Performance · Combustion characteristics · Heat-transfer parameter

1 Introduction

Transportation vehicles are among the biggest sources of emissions, emitting around 25% of the greenhouse gas pollution (GHGs) found in the environment [1], because the use of unleaded gasoline (E0) fuel in vehicles is linked to worse engine-out emissions and air quality [2]. This has challenged manufacturers and researchers to develop new modification techniques to decrease exhaust emissions and enhance engine performance [1] because even small improvements in engine efficiency, whether in the engine-out emissions or vehicle fuel economy, represent a major impact. Besides, an alternative process of reducing GHGs is to substitute or blend gasoline fuels with biofuels produced from biomass resources. Among the biofuels, bioethanol is a renewable fuel obtained from lignocellulosic biomass (LCB) materials that can be used on its own or blended with unleaded gasoline in spark-ignition (SI) engines. The physicochemical properties of bioethanol fuels are similar to conventional fuels [3]. As previously reported, bioethanol-gasoline blend fuels have more advantages than unleaded gasoline only in SI engines [4, 5], namely, lower emission levels therefore lower environmental impact [6], higher octane rating [7], higher volumetric efficiencies, and quicker combustion [8]. However, research study has been carried out on the effect of reformulated fuel on emission, performance, and combustion values of various SI engines, but less research has been conducted on modified engines.

Q et al. [9] investigated the effect of ethanol blends on engine performance such as brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), brake power (BP), and engine torque (T_E) using modified and modernized SI engines. They concluded that the BTE, T_E, and BP of the

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blends are almost similar to that of gasoline, but the BSFC of the blends is slightly higher due to the rich mixture at higher brake mean effective pressure (BMEP). Research conducted by Yussoff et al. [10] reported that carbon monoxide (CO) and carbon dioxide (CO_2) emissions in the cold phase were decreased. This occurred due to the increase in ethanol blend ratio, which also increases the latent heat of vaporization. This has the effect of reducing the lower heating value (LHV) and combustion temperature which leads to the rise of unburned hydrocarbons (HC) cold emission factors and, at the same time, to the decrease in nitrogen oxides (NO_X) cold emission levels [8]. These findings also suggest that more fuel injections from ethanol fuel are needed to compensate for decreases in engine performance [6, 11].

These findings of advanced ignition timing is a surrogate way for predicting the effect of combustion performance and has been studied by various researchers, but their findings depended on the operating parameters and engine specifications. De Melo et al. [12] examined the effect of gasoline-anhydrous ethanol (E25) on emissions and combustion using a Flex-Fuel engine. The results showed intricate trends with NO_X emission when the percentage of ethanol was added under different operating conditions and spark advance timing. Zareei et al. [13] studied the effects of variable ignition timing from 41° before top dead center (bTDC) to 10° after top dead center (aTDC) on SI performance and engine-out emission. At 10° crank angle (CA) bTDC, the result showed a significant decrease in NO_X with an increase in HC while CO_2 was the same. Thus, at 31° CA bTDC, the optimal power and torque was obtained.

In this study, bioethanol produced from *Mbwazirume* biomass peels was used as a blend fuel at different ratios (E5, E10, and E15) with unleaded gasoline. These blend fuels were tested under various engine speeds in a modernized TD201 four-stroke petrol engine, equipped with efficient electronic fuel injection (EFI) systems in order to assess engine emissions, performance, and combustion characteristics because ignition timing is an alternative process to predict engine performance. The experimental results showed significant reductions in emissions, especially regarding NO_X emissions.

2 Experimental apparatus and procedure

2.1 Engine test setup

The experiments were carried out using a TD201 four-stroke petrol engine (modern small engine), which was modified at the cylinder head and crank output shaft in order to be able to accept the optional cylinder head pressure transducer (ECA101) and crank angle encoder (ECA102). The test bed setup is illustrated in Fig. 1. The engine is powered by 8.5:1 CR, air cooled, 1-cylinder, 4-stroke with overhead valves
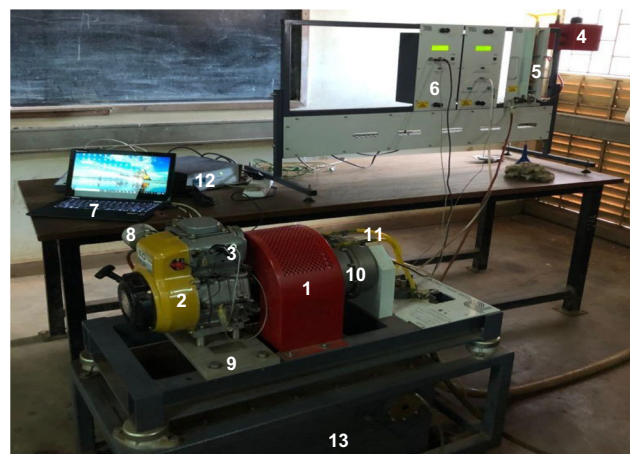
Fig. 1 The test bed setup. (1) DC dynamometer. (2) SI engine, TD201 model. (3) Transducer. (4) Fuel tank. (5) Automatic volumetric fuel gauge with DVF1. (6) Control panel. (7) Computer system with VDAS software. (8) Air inlet adapter. (9) Base plate. (10) Crank encoder. (11) Water-cooled inlet. (12) Engine cycle analyzer. (13) Exhaust gas outlet

(inlet and exhaust), governor, a carburetor fuel system, electric spark ignition, recoil starter, dummy transducer, and splash lubricator. The engine has a bore of 67 mm, stroke of 49 mm, and a crank radius of 24.5 mm. Some of these engine specifications are shown in Table 1. The engine was coupled to a dynamometer with a speed sensor for defining the proper engine speed. However, the engine power and maximum speed were regulated when the governor pressurized the carburetor to lessen the fuel-air mixture that goes into the cylinder. The amounts of CO, CO_2, NO_X, and HC emissions were metered using the Testo Flue Gas (TFG) analyzer with calibration.

2.2 Test procedure

In this study, the test fuels were prepared according to volumetric percentages. These fuels were pure gasoline (E0), and bioethanol blend ratios which contained 5%, 10%, and 15% ethanol *v/v* known as E5, E10, and E15, respectively. The engine was authorized to run a few moments until it reached steady-state conditions, after which the data (such as engine performance and engine-out emissions) were collected. These experiments were conducted at the selected operation conditions: engine speeds ranged from 1800 to 3000 rpm at 8.5:1 CR with wide open throttle (WOT) and 6.7 bar ± 0.9 bar for BMEP at low ambient temperature. An extension cable from the transducer was connected to the engine cycle analyzer in order to measure the cylinder pressure at consecutive cycles. The pressure, relative humidity, and ambient air temperature were monitored. The maximum noise levels of the engine were measured using a sound recorder at a distance of 100 cm and height of 160 cm for 2 min (see Table 2). No starting difficulties were observed with the engine when

Table 1 Engine specification

Items	Specification
Engine type	Single-cylinder, four-stroke TD201 SI engine, equipped with EFI systems
Dimensions (W × H × D)	(400 × 400 × 300 m)
Absolute maximum power	6 hp at 4000 r/min
Continues rated power	2.6 kW at 3000 r/min
	2.9 kW at 3600 r/min
Bore × stroke	67 mm × 49 mm
Crank radius	24.5 mm
Connecting rod length	85 mm
Displacement	172 cm^3
CR	8.5:1
Ambient air pressure	1018 mbar
Valves	Intake and exhaust

fueled with E5, E10, and E15. The fuel properties of the test fuels used in this work are presented in Table 3 as previously presented in our article [3]. The details about the experimental process can be obtained in previous research [14–16].

3 Results and discussion

3.1 Performance behaviors

3.1.1 Effect of specific fuel consumption (SFC) and BTE

These experiments were conducted at various engine speeds for a certain percent of the WOT using constant 8.5:1 CR. Figure 2 reveals the relations between engine speed and SFC for various fuel blends. When the engine speed increased from 2400 to 2700 rpm, the SFC for E5 and E15 decreased by 11.3% and 15.7% respectively, which was lower than that of unleaded gasoline and E10. It was observed that the engine appeared to operate at the highest SFC within 58 to 74% WOT while fueled with E10. In this case, there was an uncertain trend. However, this result shows that the SFC was relatively

Table 2 The maximum noise levels measured

Record positions	Altitude recording dB(A)[#]
At machinist ear	90
In front of the engine[*]	90
Back of machine[*]	90
Left-hand side of machine[*]	91
Right-hand side of machine[*]	94
Localized areas of excess noise	102

[#] At Leq period (2 min); [*] at a distance of 100 cm and height of 160 cm

Noise pressure levels: At 80 dB(A), the ear defenders are worn and < 85 dB(A), the ear defenders should be neglected

low at 2400 rpm with E15, which disagrees with recent work by Phuangwongtrakul et al. [17], who stated that at low engine speed, the SFC is relatively high. However, several researchers reported that the SFC can either decrease or increase with bioethanol fuel. These conflicts occur for several reasons: when the SFC decreases, the combustion efficiency increases with the effect of oxygen content [15]; the SFC decreases, reaching its minimum values when the BTE increases [18]; and higher due to the rich mixture at higher BMEP [9] and lower heating value [4]. These results are viable for lower mixtures of bioethanol, but there is no evidence from the literature that fully describes a decrease in SFC for high bioethanol blends. In addition, this research provides a detailed summary and comparison of the recent trends for both increased and decreased SFC.

Figure 3 presents the effect of BTE for bioethanol fuel blend under steady-state conditions at full load. The engine attained a maximum efficiency of 25.7% at E15 with 2700 rpm; this is higher by 6.7% compared to pure gasoline, which seems to be the optimum. At all the engine speeds, E5 and E10 showed a slight decrease in engine efficiency, but the engine ran smoothly without any additional noise. This may be attributed to fuel enrichment or spark retard. It was suggested that increase in CRs enhances thermodynamic expansion efficiency, despite the fact that a few theoretical gains are lost due to the increment of ring-

Table 3 The fuel properties of bioethanol and gasoline

Property	Units	Bioethanol	Gasoline
Composition (C, H, O)	Mass %	52, 13, 35	86, 14, 0
Density at 15 °C	Kg/m	793.2	737
LHV	MJ/kg	26.3	43.5
Colorific value	MJ/kg	29.1	47.3
Viscosity at 20 °C	mm^2-s^{-1}	1.3	0.37 to 0.44
Flash point	°C	21.7	− 45 to − 13
Ethanol content	%vol	90.19	-
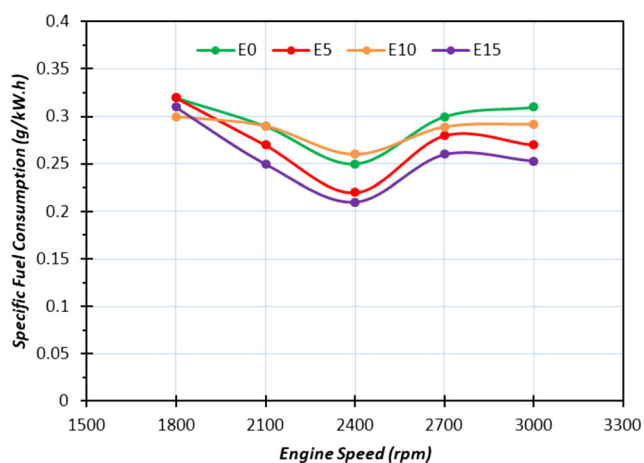
Fig. 2 The effect of bioethanol blend ratio at CR = 8.5:1 on specific fuel consumption

to-bore wall friction from higher cylinder pressures. The trend towards lowering of parasitic losses in driving the high pressure fuel pump may provide an effective path for reducing friction [19]. Minimizing friction in the engine is an essential way for decreasing fuel consumption.

3.1.2 Effect of power and torque

Figure 4 indicates the engine power which operates at 5%, 10%, and 15% *v/v* bioethanol under different engine speeds. As observed, the engine power using bioethanol-gasoline blends was slightly higher by 1.3%, 1.9%, and 2.4% with E5, E10, and E15, respectively, compared to E0. This occurred as a result of an increase in engine speeds and the low caloric value of the bioethanol blends compared to gasoline. These results indicated that the high octane number in bioethanol blends improved the combustion properties under all engine speeds at steady-state conditions. Other properties that favored the decrease in fuel consumption and increase in engine power were as follows: high density, high LHV,
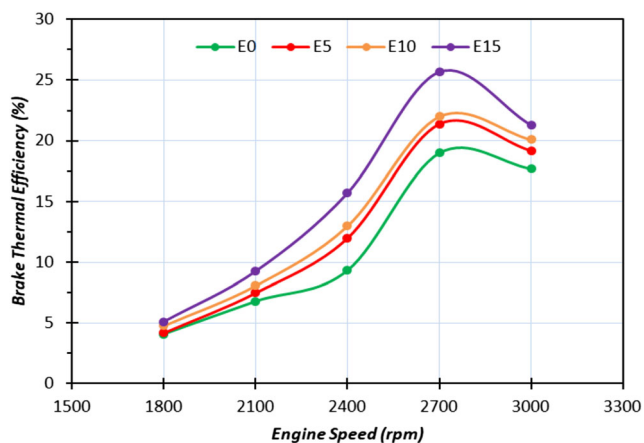
Fig. 3 The effect of bioethanol blend ratio at CR = 8.5:1 on BTE
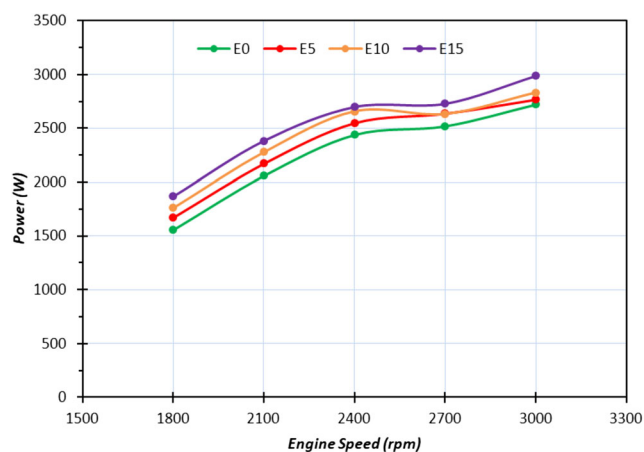
Fig. 4 The effect of bioethanol blend fuels at various engine speeds for CR = 8.5:1 on power

extended limits of flammability, the number of molecules being more than the reactants, and constant boiling temperature.

Figure 5 shows the effect of various bioethanol blend ratios on T_E at various engine speeds. The result shows that the optimal T_E performance was obtained between 2400 and 2700 rpm for all fuel types and the lowest value was found between 1800 and 3000 rpm. When the bioethanol ratio increased, the T_E increased at certain engine speeds, and then the engine-out emission also increased. The T_E and BMEP for all blend fuels were higher than E0 at an engine speed of 2400 to 2700 rpm. This happens because there is less time to complete combustion in an engine cycle, which requires faster flame speed with an increase in ignition timing [6].

3.2 Combustion characteristics

3.2.1 Heat-transfer and combustion model

The loss of heat by the combustion chamber wall (Q_h) is one of the key heat losses in an ICE, and is calculated using
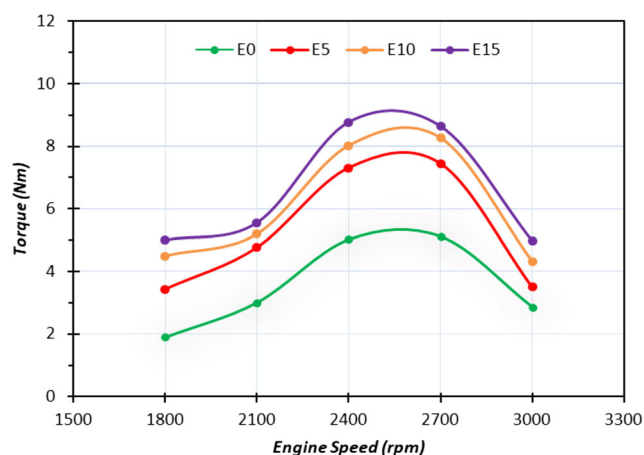
Fig. 5 The effect of bioethanol blend fuels at various engine speeds for CR = 8.5:1 on torque (T_E)

internal heat balance in an engine process simulation [20], as shown in Eq. 1. The unaccountable heat loss Q_u for the mixture-controlled combustion is the heat supplied by fuel minus cumulative heat taken by fluid properties (cooling water, exhaust gases, and lubricant oil) and piston power, as given in Eqs. 2 and 3. This model is used to predict the heat loss and combustion characteristics in SI engines. Duc [21] developed a simulated model based on a test engine using the first law of thermodynamics to predict the high-pressure cycle and combustion characteristics in the internal energy in an ICE. However, the model neglected the effect of heat taken by lubricant oil on the internal heat balance of the engine. The thermal properties of lubricant oil are a significant factor, allowing the oil to transfer heat from the engine. The larger the specific heat and thermal conductivity, the more efficient is the transfer of heat by the oil [22]. In this study, we developed a model that considers the effect of heat taken by engine oil, piston power (P_ω), heat input by fuel, heat taken by cooling water, and exhaust gases.

$$Q_h = \frac{1}{\omega} \int_c^l h \times A \cdot (T_w - T_s) \times d\varphi \tag{1}$$

where A is the instantaneous combustion chamber surface area, c is the over the combustion cycle, $(T_w - T_s)$ is the temperature difference of the wall-gas, φ is the crank angle, ω is the angular frequency, h is the heat transfer co-efficiency.

$$Q_u = \dot{m}_f C_{vf} - \sum_{n=1}^{k} Q_n \tag{2}$$

$$Q_u = \underbrace{\dot{m}_f \times C_{vf}}_{\text{fuel heat input}}$$

$$- \left[P_\omega + \underbrace{\dot{m}_w C_w (T_{out} - T_{in})}_{\text{cooling water}} + \underbrace{(\dot{m}_a + \dot{m}_f) C_{pg} (T_{ext} - T_{atm})}_{\text{exhaust gases}} + \underbrace{\dot{m}_o C_o \Delta T}_{\text{oil}} \right] \tag{3}$$

The periodicity of a one-dimensional transient temperature and the temperature oscillation on the combustion chamber wall expands infinitely in one direction as the starting point. The wall heat flux densities that cause the temperature behaviors which can be calculated using Laplace's differential equation formulated by Eichelberg (Eq. 4), as reported by Pinkernell et al. [23]. The authors [23] also suggested a potential way to correct the effect of deposits (soot, carbon, etc.) using soot free model fuels.

$$\dot{q} = \dot{q}_m$$

$$+ \lambda \cdot \sum_{i=1}^{\infty} \sqrt{\frac{i\omega}{2a}} \cdot [(X_i + Y_i) \cdot \cos(i\omega t) + (Y_i + X_i) \cdot \sin(i\omega t)] \tag{4}$$

However, h can be calculated using Eq. 5, which was formulated by Woschni for high-pressure cycles in combustion engines. Equation 5 depends on velocity, combustion pressure, and gas temperature with respect to time for which the burned gas on thermal. Also, it reveals the amount of NO_X formation rate produced during combustion.

$$h_w = 130 \times D^{-0.2}$$

$$\times T_s^{-0.53} \cdot P_s^{0.8} \left[C_1 \times c_m + \underbrace{C_2 \left(\frac{V_h \cdot T_1}{P_1 \cdot V_1} \right) (P - P_{wo})}_{\text{Combustion term}} \right]^{0.8} \tag{5}$$

where P_{wo} is the motored engine cylinder pressure; C_m is the mean piston velocity; C_1 is swirl quantity for the flow velocity: when the intake closes from exhaust opens, the $C_1 = 6.18 + 0.417(c_u/c_m)$, and when the exhaust opens from intake closes, the $C_1 = 2.28 + 0.308(c_u/c_m)$; $C_2 = 0.00324$ (m/sK) for direct-ignition engines, $C_2 = 0.0062$ (m/sK) for engines with different combustion chambers, and $C_2 = 0$ for compression and gas exhaust; P_1 is the cylinder pressure at the beginning of compression; D is the cylinder diameter; V_h is the swept volume; T_s is the gas temperature in the cylinder.

3.2.2 Combustion analysis

Figure 6 shows the heat release rate, combustion duration, and ignition delay with respect to crank angle (φ/°CA) under various blended fuels. When the engine operated with E15, no deterioration was observed, and hence exhibited high indicated power and efficiency with low fuel consumption between 12 and 18° CA aTDC. These are due to the low content of carbon in bioethanol which eliminates the occurrence of soot formation and requires less air to burn a fuel blend with low luminosity and radiation. The results also showed a reduction
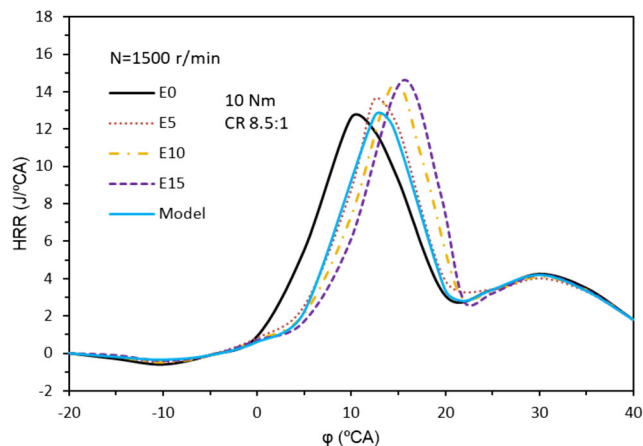
Fig. 6 Variation of rate heat transfer for different bioethanol blends at 1500 rpm with 10 Nm

in air pollution (NO$_X$ emission) produced by lead (pb) and heat loss when fueled with E10 and E15 at low flame temperature. Figure 5 shows that E5, E10, and E15 fuels had a higher premixed combustion duration with a decrease in controlled diffusion combustion compared to unleaded gasoline due to their longer ignition delay time [24]. These phases have faster combustion because the blend fuels burn at the same time with various φ (°CA) increases of ignition delay [25]. Thus, it was observed that increases in cycle efficiency shortened the combustion duration.

As illustrated in Fig. 7, the in-cylinder pressure was slightly higher for E0 at 15° CA aTDC, which had a beneficial influence on the auto-ignition timing. This occurred due to there being less heat loss through combustion chamber wall conduction and flame radiation. The predicted models of the combustion characteristics under different operational conditions showed similar trends to the actual results, as illustrated in Figs. 5 and 6. At 20° CA bTDC, in early injection conditions, the fuel ignition started to burn simultaneously at 0° CA aTDC. This is because the blend fuels evaporated rapidly which led to formation of a homogeneous mixture quickly during the short ignition delay. When the combustion phases were the same, the model results suggested that a little modification in the heat transfer parameter has a great impact on the thermal efficiency. These combustion characteristics have a direct effect on engine-out emissions, especially NO$_X$ emissions which are associated with combustion temperature [26].

It was observed that high engine speeds increased fuel dilution which led to slight reduction in lubricant oil viscosity. The increase in premixing ratio yielded a slight increase in cylinder pressure of the E0 premixing fuel, but the difference was small compared to E5, E10, and E15 premixing due to the small imbalance among all ignition timing. The ignition delay uniformly increased when the injection timing proceeded from 3 to 6° CA aTDC. This increase was because of low temperature and pressure in the combustion chamber. As
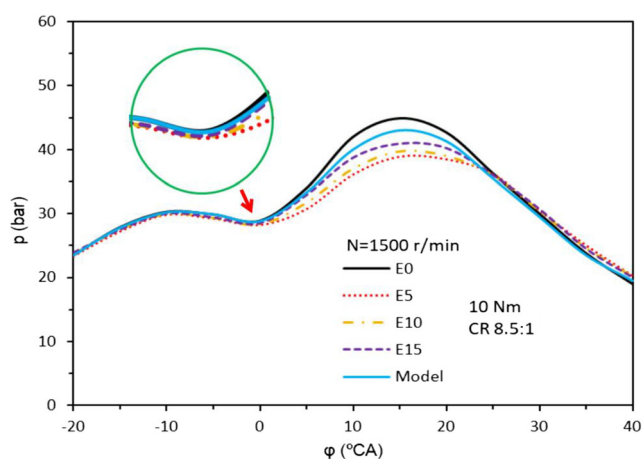
previously reported, the decrease of pressure and temperature in the combustion chamber is due to the descent of the piston after injection or during injection [27]. Figure 8 shows the effect of fuel blend on IMEP for the start of injection (SOI) SOI° CA aTDC. It was observed that the engine power increased as the injection timing approached top dead center (TDC). The increase in bioethanol fraction induced an increase in IMEP for all injection timings.

3.3 Emission characteristics

3.3.1 Effect of NO$_X$ emissions

As shown in Fig. 9, it was observed that CO was highest with E5 and NO$_X$ emission was lowest with E10 fuel. This can be explained because the higher the LHV, the lower the combustion temperature. In addition, the percentage of S, N, and ash content was relatively low in the biomass fuel. These suggest that the bioethanol fuel extracted from *Mbwazirume* biomass does not need any processing or technology for reducing the exhaust emission of sulfur oxides (SO$_X$) and NO$_X$ [28]. Besides, the engine showed an interesting trend for attaining a maximum efficiency at E15 with a decrease of 15.7% in fuel consumption compared to that of E0. This shows that bioethanol blends improved fuel economy, so if the bioethanol is affordable, the economics will be favorable.

Emission characteristics such as HC, CO, CO$_2$, and NO$_X$ of bioethanol fraction combustion are presented in Fig. 10, 11, and Fig. 12. In the case of SOI for NO$_X$ emissions, the trend followed the bioethanol fraction and φ (°CA) very closely. Figure 9 shows the NOx emission behavior of combustion for the bioethanol fraction with respect to SOI° CA aTDC. It was observed that the rate of pressure was relatively less due to the low fueling rate of the bioethanol injection, which was enough to obtain robust injection and combustion. This small amount of the injected fuel involved in the combustion phase caused a low NO$_X$ emission and temperature. The rate of NO$_X$
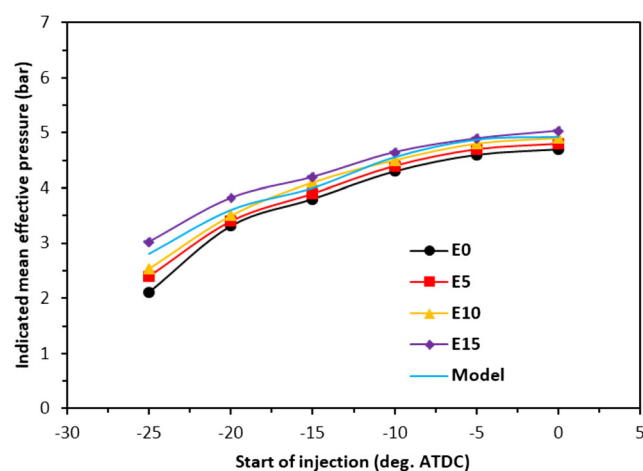

Fig. 7 Variation of pressure for various blended fuels at CR 8.5:1 with 10 Nm

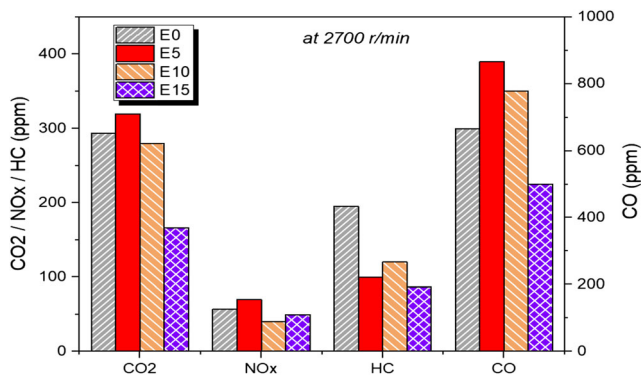Fig. 8 The effect of blend fuels on IMEP for SOI° CA aTDC

Fig. 9 The impact of bioethanol ratios on emissions at constant engine speed (2700 rpm) with CR = 8.5:1

formation rose higher with E5 and E10 due to the combustion advanced which led to high temperature and in-cylinder pressure compared to the E0 and E15. The NO_X emissions in this study were low compared to those presented in the literature using E5 and E10 [29], E20, E50, E75, and E100 [30] and bioethanol-biodiesel combustion [31].

3.3.2 Effect of CO, CO_2, and HC emissions

The purpose of this section is to highlight some significant aspects of exhaust emissions associated with blended fuels in EFI engine. The CO, CO_2, and HC emissions generated by road vehicles are increasing significantly worldwide. According to the foregoing conclusion, the engine-out emissions can either increase or decrease significantly. The effect of engine speeds of 2700 rpm on CO, CO_2, and HC emissions were studied at all blend fuels, as shown in Fig. 9. The result from this experiment shows that the proportion of CO_2 reduced as the blend ratio increased. This happens due to the oxygen amount in the blend fuels and the high flammability limit which improved the mixing process and hence combustion efficiency [6]. This result is similar that of Iodice et al. [8].
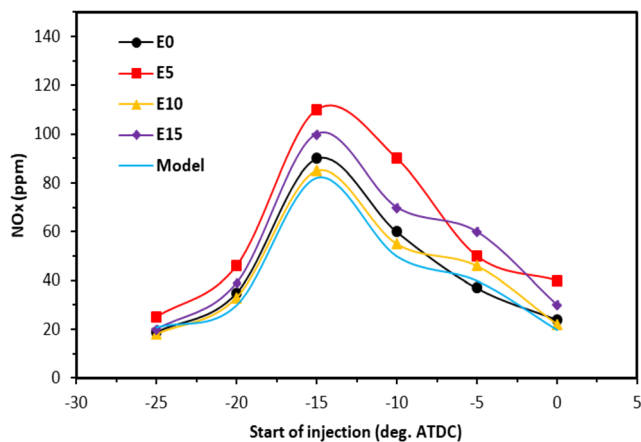
Fig. 10 The NO_X emission variations for bioethanol fraction with respect to SOI° CA aTDC
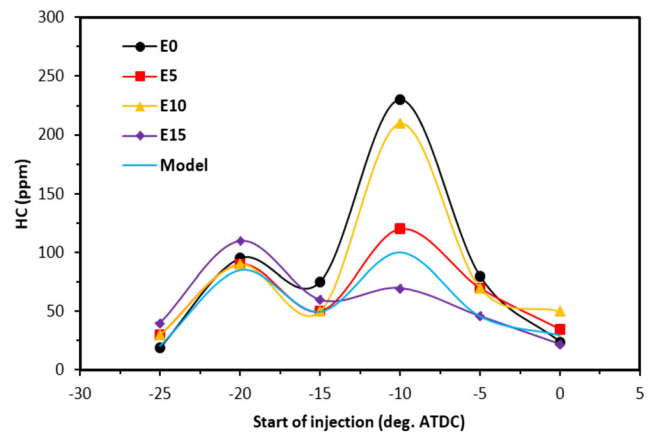
Fig. 11 Effect of HC emissions variations for bioethanol fraction with respect to SOI° CA aTDC

As shown in the Fig. 9, the E5 fuel produced the highest emissions of CO and CO_2 while the lowest emissions of CO, CO_2, and HC occurred with the E15 fuel. This effect is due to the increase in the actual air-fuel ratio which decreases the stoichiometric air-fuel ratio of the blend fuels as a result of the high oxygen content in the bioethanol [32]. As illustrated in Figs. 11 and 12, low emissions of CO and HC were observed when the injection timing was retarded towards TDC. The CO emission decreased from 160 to 93 ppm with an increase in SOI (between 15° CA bTDC and CA0) with E15. This trend of variation is similar to that of the model, but at 2700 rpm, the CO emission was higher (see Fig. 9) due to the shorter combustion time at high engine speed [33]. Figure 11 reveals that the HC emission for the SOI decreased as the blend fuels increased. The lowest HC emissions occurred when the SOI retarded, except at 10° CA bTDC/SOI which did not follow this trend.

CO emissions occur when the engine cylinder undergoes incomplete oxidation of the fuel, which is also sensitive to the temperature for homogenous combustion of lean mixtures. Figure 11 reveals the increase and decrease in the combustion chamber with respect to temperature. The CO
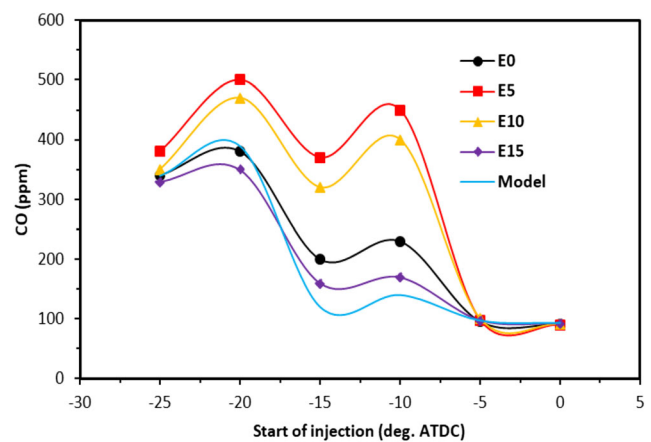
Fig. 12 The CO emissions variations for bioethanol fraction with respect to SOI° CA aTDC

emissions decreased with E15 and increased rapidly for E5 and E10 compared to E0, when the T_{eg} was at 192 °C for 21.7-s fuel drain time (F_{dt}). This occurs due to the combustion temperatures at very dilute conditions being too low to complete the CO-to-CO_2 reactions before quenching due to expansion cooling [34].

4 Conclusion

Better results can be obtained from SI engines using bioethanol in terms of performance, combustion behaviors, and emissions; this depends on operating conditions and properties of bioethanol-gasoline blends which create significant changes in the combustion system. The conclusions are as follows.

1. When the engine operated with E10 and E15, the engine-out emissions decreased while the engine performance slightly increased. These results suggest that the fuel blend ratios induced an increase in combustion duration with minimum premixing combustion duration, hence exhibited low emissions, high indicated power, and efficiency with low fuel consumption (at 12 to 18° CA aTDC). In addition, rapid evaporation of the fuel blend was observed thus leading to formation of a homogeneous mixture quicker during short ignition delay.

2. The rate of NO_X formation rose higher with E5 and E10; this is due to the combustion advanced which led to higher temperatures and in-cylinder pressures than that of E0 and E15 fuel. CO and CO_2 emissions decreased with E15 and rapidly increased with E5 and E10 while the HC emissions decreased at all injection timings for E5, E10, and E15, except that of 10° CA bTDC/SOI which did not follow this trend.

3. High engine speed increased fuel dilution which led to a slight reduction in lubricant oil viscosity. As critically analyzed, this might produce wear in the future.

4. The predicted model of the combustion characteristics showed the same consistent behavior which the experimental results found. Also, when the combustion phases were the same, the model results suggested that a little modification in the heat transfer parameter has a great effect on the thermal efficiency.

5. The literature suggests that a possible way of correcting the effect of deposits (soot, carbon, etc.) is to use soot free model fuels (as discussed in Section 3.2).

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Chapter 9

Conclusion and Recommendation for Future Works

Conclusion and Recommendation for Future Work

9.1 Conclusion

The aims and objectives of this study were to characterize the biomass, evaluate and produce bioethanol fuels from a unique LCB which is the *matooke* peels species, and examined the emissions and combustion effects of low content rates of bioethanol blends with gasoline in a modernized SI engine. Utilizing this waste biomass for bioethanol production through a biotechnological process not only helps to reduce environmental pollution but can also reduce the dependence of Uganda on oil-producing countries and provide an additional source of income for the government.

The *matooke* peels species such as *Mbwazirume* and *Nakyinyika* biomass peels were characterized to identify its use in bioenergy production. Experimental findings revealed that the pretreated *Mbwazirume* biomass exhibited excellent solid fuel properties when compared to untreated *Mbwazirume*, and pretreated and untreated *Nakyinyika* biomass peels. The physical and chemical properties of the bioethanol produced are within the acceptable range of ASTM standards and comparable to gasoline. The *Mbwazirume* biomass shows high bioethanol yields and excellent fuel properties, thus can serve as a fuel of choice for further experimentation. With the background of practical and policy implications presented in section 5.7 of paper 5, it was found that the renewable energy policy (REP) 2007 was the appropriate policy for this research finding.

This study shows that the use of bioethanol in an SI engine has the advantage of reducing most regulated engine-out emissions, as well as improving combustion and thermal efficiency. This impact changes with the blend ratio. When the engine operated with E10 and E15, the engine-out emissions decreased while the engine performance slightly increased. These results suggest that the fuel blend ratios induced an increase in combustion duration with minimum premixing combustion duration, hence exhibited low emissions, and high indicated power and efficiency with low fuel consumption at 12º CA aTDC to 18º CA aTDC. The rate of NO_X formation increased with E5 and E10 which would have been due to the combustion advanced which led to higher temperatures and in-cylinder pressures than that of E0 and E15 fuel. CO and CO_2 emissions decreased with E15 and rapidly increased with E5 and E10 while the HC emissions decreased at all injection timings for E5, E10, and E15, except that of 10º CA bTDC/SOI which

did not follow this trend. However, contrary to assumptions, there is no linear trend between increasing bioethanol content and any change in combustion and heat transfer characteristics. The predicted model of the combustion characteristics showed the same consistent behavior with the experimental results found. The model results suggested a little modification in the heat transfer parameter has a great effect on the thermal efficiency, especially with E5 and E10 blend fuels. E15 demonstrated the most essential fuel for increasing combustion speed and decreasing heat losses to coolant and exhaust.

9.2 Recommendation for Future Work

Bioethanol is an alternative fuel obtained from biomass and has been used in different countries for several years as it is considered to be renewable and clean energy. The major problem of bioethanol is the availability of biomass materials for its production, and not all bioethanol fuels bring benefits to the environment concerning performance and emissions. Assessment needs to be made for each type of biomass material, location, and extraction technique. In addition, better results can be obtained from spark-ignition engines using bioethanol in terms of performance, combustion behaviors and emissions in relation to operating conditions and properties of bioethanol-gasoline blends which create significant changes in the combustion system. The engine experiment presented in this thesis concentrates on the effect of low content bioethanol blends on the emissions, combustion characteristics and heat transfer behavior at low ambient temperature and selected operating conditions. Future research may investigate the effect of high percentage bioethanol blends on port-fuel injection or wall-guided DISI engines with different compression ratios at high ambient temperature and different operation conditions, which is of extreme importance. The sensitivity of bioethanol to all these changes should be properly investigated. In addition, the higher heating value (HHV) of the biomasses was found to be between 15.52 MJ-kg^{-1} and 18.28 MJ-kg^{-1}. According to EN ISO 16559 standard solid biofuel terminology, the total waste generated per capita per year with this HHV can produce an electric power of 100 kWh to 186.52 kWh which is more than enough for consideration as a source of energy. It is suggested that the prospective research should also focus on *Nakyinyika* biomass and other species for reaching Ugandan bioenergy's targets over the medium to long term, for the purposes of electricity generation, since electricity distribution in Uganda is among the lowest in Africa.

Appendixes

Appendix I: Editing Certificates

Appendix A: Introduction and Conclusion

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EDITING CERTIFICATE

Re:**Abdulfatah Abdu Yusuf**
For editing of the Introduction and Conclusion of PhD thesis

I confirm that I have edited these pages for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology).

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22 September 2019
per email

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Re: **Abdulfatah A. Yusuf**
Journal article: **Bioethanol production from different lignocellulosic biomass as alternative fuel for spark-ignition engines: A comprehensive review**

I confirm that I have edited this article and the references for clarity, language and layout. I am a freelance editor specialising in proofreading and editing academic documents. I returned the document to the author with track changes so correct implementation of the changes in the text and references is the responsibility of the author. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology). During my 13 years as a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology I supervised numerous Master's degree dissertations.

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06 June 2018
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Journal article: **Effect of cold start emissions from gasoline-fueled engines of light-duty vehicles at low and high ambient temperatures: Recent trends**

I confirm that I have edited this article and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology). During my 13 years as a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology I supervised numerous Master's degree dissertations.

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EDITING CERTIFICATE

Re: **Abdulfatah Abdu Yusuf**
Journal article: **Characterization of Ugandan biomass wastes as the potential candidates towards bio-energy production**

I confirm that I have edited this article (excluding the references) for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology). During my 13 years as a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology I supervised numerous Master's degree dissertations.

Dr Richard Steele
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EDITING CERTIFICATE

Re: **Abdulfatah A. Yusuf**
For editing journal article: **Comparative study on pyrolysis and combustion behavior of untreated Matooke biomass wastes in East Africa via TGA, SEM, and EDXS**

I confirm that I have edited this article for clarity, language and layout. I did not edit the references. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years.

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EDITING CERTIFICATE

Re: **Yusuf Abdulfatah Abdu**
Journal article: **Bioethanol production from different *Matooke* peels species in Uganda: A future alternative fuel for spark-ignition engine**

I confirm that I have edited this article and the references for clarity, language and layout. I am a freelance editor specialising in proofreading and editing academic documents. I returned the document to the author with track changes so correct implementation of the changes in the text and references is the responsibility of the author. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology). During my 13 years as a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology I supervised numerous Master's degree dissertations.

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Journal article: **Effect of low bioethanol fraction on emissions, performance and combustion behavior in a modernized electronic fuel injection engine**

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Dr Richard Steele
10 June 2019
per email

Appendix II: Acceptance Letters

Appendix: Paper 1

Official Acceptance of Research Paper

Paper ID: IJMET/10/04/2019/IJMET_42638　　　　　　**Date:** 21-March-2019

Dear **Abdulfatah Abdu Yusuf and Freddie L. Inambao**

We would like to inform you that your paper titled **"Bioethanol production techniques from lignocellulosic biomass as alternative fuel: A review"** has been accepted for publication in **International Journal of Mechanical Engineering and Technology (IJMET),** Volume 10, Issue 04, (April 2019) issue of the journal based on the Recommendation of the Editorial Board without any major corrections in the content submitted by the researcher.

This letter is the official confirmation of acceptance of your research paper.

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Your research paper will be appearing in IJMET, Volume 10, Issue 04, April 2019.

International Journal of Mechanical Engineering and Technology (IJMET)
Journal Impact Factor (2019): 10.6879 Calculated by GISI
ISSN Print:　0976 – 6340
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Appendix: Paper 2

International Journal of Ambient Energy - Decision on Manuscript ID TAEN-2018-0352.R1

3 messages

International Journal of Ambient Energy <onbehalfof@manuscriptcentral.com>   Sun, Sep 23, 2018 at 7:51 PM
Reply-To: nj.hewitt@ulster.ac.uk
To: abdulfatahabduyusuf@gmail.com

23-Sep-2018

Dear Mr Yusuf:

Ref: Progress in alcohol-gasoline blends and their effects on the performance and emissions in SI engines under different operating conditions

Our reviewers have now considered your paper and have recommended publication in International Journal of Ambient Energy. We are pleased to accept your paper in its current form which will now be forwarded to the publisher for copy editing and typesetting. The reviewer comments are included at the bottom of this letter, along with those of the editor who coordinated the review of your paper.

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Thank you for your contribution to International Journal of Ambient Energy and we look forward to receiving further submissions from you.

Sincerely,
Dr Hewitt
Editor in Chief, International Journal of Ambient Energy
nj.hewitt@ulster.ac.uk

Reviewer(s)' Comments to Author:

Reviewer: 1

Comments to the Author
Accept in the present form

Editor's Comments to Author:

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Abdulfatah Abdu Yusuf <abdulfatahabduyusuf@gmail.com>   Sun, Sep 23, 2018 at 9:07 PM
To: Freddie Inambao <Inambaof@ukzn.ac.za>

Appendix: Paper 3

Your manuscript CSITE_2018_429_R1 has been accepted

1 message

Huihe Qiu (Case Studies in Thermal Engineering) <EviseSupport@elsevier.com>   Sat, Feb 16, 2019 at 5:43 PM
Reply-To: meqiu@ust.hk
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Ref: CSITE_2018_429_R1
Title: Effect of cold start emissions from gasoline-fueled engines of light-duty vehicles at low and high ambient temperatures: Recent trends
Journal: Case Studies in Thermal Engineering

Dear Mr. Yusuf,

I am pleased to inform you that your paper has been accepted for publication. My own comments as well as any reviewer comments are appended to the end of this letter.

Your accepted manuscript will now be transferred to our production department. We will create a proof which you will be asked to check. You can read more about this here. Meanwhile, you will be asked to complete a number of online forms required for publication. If we need additional information from you during the production process, we will contact.

Thank you for submitting your work to Case Studies in Thermal Engineering. We hope you consider us again for future submissions.

Kind regards,

Huihe Qiu
Editor-in-Chief
Case Studies in Thermal Engineering

Comments from the editors and reviewers:
- Reviewer 1

-

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Appendix: Paper 4

KIU
EXPLORING THE HEIGHTS

Yusuf Abdulfatah <yusuf.abdulfatah@kiu.ac.ug>

Your Submission

1 message

Renewable & Sustainable Energy Reviews <eesserver@eesmail.elsevier.com>   Mon, Oct 7, 2019 at 7:33 AM
Reply-To: Renewable & Sustainable Energy Reviews <rser@elsevier.com>
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Cc: nizami_pk@yahoo.com, anizami@kau.edu.sa, inambaof@ukzn.ac.za

Ms. Ref. No.: RSER-D-19-01792R3
Title: Characterization of Ugandan biomass wastes as the potential candidates towards bioenergy production
Renewable & Sustainable Energy Reviews

Dear Mr. Abdulfatah Abdu Yusuf,

I am pleased to inform you that your article has been accepted for publication in Renewable & Sustainable Energy Reviews (RSER). Below are any outstanding comments from the Editor and reviewer(s). These may require your attention. You will also be receiving a number of communications from us shortly regarding the publication process.

First, your accepted manuscript will be transferred to our Production Department and work will begin on creation of your 'proof.' If any additional information is required to produce your proof the RSER team will contact you. If no further details are required, you will receive an email in the next few days (depending on the Production Department workload) with a request to approve your proof and to complete a number of online Elsevier forms. Use this proof for checking the typesetting, editing, completeness and correctness of the text, tables and figures. No other significant changes may be made to the article as accepted for publication at this stage. It is important to ensure that all corrections are sent back to the Production Department in one communication. Proofreading is solely the responsibility of the corresponding author. Therefore you must check your proof carefully before replying, as inclusion of any subsequent corrections cannot be guaranteed.

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Finally, congratulations on getting your article accepted for publication in RSER.

Yours sincerely,

Abdul-Sattar Nizami, PhD, MSc.(Eng.), BSc (Hons.)

Appendix: Paper 5

Appendix: Paper 6

Abdulfatah Abdu Yusuf <abdulfatahabduyusuf@gmail.com>

Your manuscript CSITE_2018_316_R1 has been accepted

1 message

Huihe Qiu (Case Studies in Thermal Engineering) <EviseSupport@elsevier.com>   Sun, Nov 18, 2018 at 6:25 PM
Reply-To: meqiu@ust.hk
To: abdulfatahabduyusuf@gmail.com

Ref: CSITE_2018_316_R1
Title: Bioethanol production from different Matooke peels species: A surprising source for alternative fuel
Journal: Case Studies in Thermal Engineering

Dear Mr. Yusuf,

I am pleased to inform you that your paper has been accepted for publication. My own comments as well as any reviewer comments are appended to the end of this letter. Now that your manuscript has been accepted for publication it will proceed to copy-editing and production.

Thank you for submitting your work to Case Studies in Thermal Engineering. We hope you consider us again for future submissions.

Kind regards,

Huihe Qiu
Editor-in-Chief
Case Studies in Thermal Engineering

Comments from the editors and reviewers:
- **Reviewer 1**

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Appendix: Paper 7

BCAB: Your manuscript entitled Effect of low bioethanol fraction on emissions, performance and combustion behavior in a modernized electronic fuel injection engine

1 message

Martin Kaltschmitt <em@editorialmanager.com>   Wed, Sep 18, 2019 at 5:29 PM
Reply-To: Martin Kaltschmitt <kaltschmitt@tu-harburg.de>
To: Abdulfatah Abdu Yusuf <yusuf.abdulfatah@kiu.ac.ug>

CC: kaltschmitt@tu-harburg.de, "Freddie L. Inambao" inambaof@ukzn.ac.za

Ref.: Ms. No. BCAB-D-19-00276R1
Effect of low bioethanol fraction on emissions, performance and combustion behavior in a modernized electronic
fuel injection engine
Biomass Conversion and Biorefinery

Dear Dr. Yusuf,

I am pleased to tell you that your work has now been accepted for publication in Biomass Conversion and
Biorefinery.

Thank you for submitting your work to this journal.

With kind regards

Martin Kaltschmitt
Editor-in-Chief
Biomass Conversion and Biorefinery

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