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Transforming Corn Stover to Useful Transport Fuel Blends in Resource-Limited Settings

Nicholas Munu

Makerere University, Uganda

Noble Banadda

Makerere University, Uganda

Nicholas Kiggundu

Makerere University, Uganda

Ahamada Zziwa

Makerere University, Uganda

Isa Kabenge

Makerere University, Uganda

See next page for additional authors

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Authors

Nicholas Munu, Noble Banadda, Nicholas Kiggundu, Ahamada Zziwa, Isa Kabenge, Jeffrey Seay, Robert Kambugu, Joshua Wanyama, and Albrecht Schmidt



Transforming corn stover to useful transport fuel blends in resource-limited settings



Nicholas Munu^{a,b,c,*}, Noble Banadda^{a,d}, Nicholas Kiggundu^a, Ahamada Zziwa^a, Isa Kabenge^a, Jeffrey Seay^{a,e}, Robert Kambugu^a, Joshua Wanyama^a, Albrecht Schmidt^{f,g}

^a Department of Agricultural and Biosystems Engineering, Makerere University, P.O. Box 7062, Kampala, Uganda

^b Department of Crop Production and Management, Busitema University, Arapai Campus, P.O. Box 203, Soroti, Uganda

^c Department of Mechanical Engineering, Ndejje University, P.O. Box 7088, Kampala, Uganda

^d Department of Agricultural and Biosystems Engineering, Iowa State University, 1340 Elings Hall, Ames, IA 50011 – 3270, USA

^e Department of Chemical and Materials Engineering, University of Kentucky, Paducah, KY 42002, USA

^f Christliche Fachkräfte International, Wächterstraße 3, 70182 Stuttgart, Germany

^g Energy Research & Development Centre, Ndejje University, P.O. Box 7088, Kampala, Uganda

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ABSTRACT

Development of local technologies is crucial to the sustainable energy agenda in resource-limited countries and the world. Strengthening local green technologies and promoting local utilization will reduce carbon emissions that could be generated during transportation and delivery of green products from one country to another. In this paper we developed bio-oil/diesel blends using a low-tech pyrolysis system designed for smallholder farmers in developing countries and tested their appropriateness for diesel engines using standard ASTM methods. Corn stover retrieved from smallholder farmers in Gayaza, Uganda were pyrolyzed in a batch rocket stove reactor at 350 °C and liquid bio-oil harvested. Bio-oil chemical composition was analyzed by Gas Chromatography equipped with Flame Ionization Detector (GC-FID). Bio-oil/diesel emulsions in ternary concentrations 5%, 10% and 20% bio-oil weight were developed with 1% concentration of sorbitan monolaurate as an emulsifier. The bio-oil/diesel emulsions and distillates had property ranges: specific gravities at 15 °C 827.4–830.7 kg m⁻³, specific gravities at 20 °C 823.9–827.2 kg m⁻³, kinematic viscosities at 40 °C 3.01–3.22 mm²/s, initial boiling points 140–160 °C, final boiling points 354–368 °C, and calculated cetane indexes 56.80–57.63. These properties of the bio-oil/diesel blends and their distillates compare well with standard transportation diesel fuel. The emulsion distillates meet the standard requirements for automotive diesel in East Africa.

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1. Introduction

The current energy and climate change challenges demand quick transition to a renewable energy path. Upsurge in global population, urbanization, standard of living, and transportation signal depletion of world's fossil fuel reserve in the near future (Ogunkunle and Ahmed, 2019; Capellán-Pérez et al., 2014; Shafiee and Topal, 2009; Dresselhaus and Thomas, 2001). This concern coupled with the fact that fossil fuels emit large quantities of primary greenhouse gases CO₂, CO, NO_x and unburnt HCs (Shekofteh et al., 2020; Heidari-Maleni et al., 2020) that

catapult global warming contextualizes recent expansion in alternative fuel research (Kumar et al., 2020a; Karmee, 2016). Currently, however, fossil fuel provides 76% of world's energy supply (Olivier et al., 2017) and is expected to be the lead energy source for the foreseeable future (Dresselhaus and Thomas, 2001). It is anticipated that global transition to cleaner energies with lower carbon footprint will be gradual and present strategy consists in consistently lowering and replacing fossil fuel content of energy carriers with cleaner renewable contents. One approach fuel scientists are exploring is blending petroleum fuels with alternative fuels in order to decrease fossil fuel dependence and enhance alternative fuel utilization in the present transportation fuel infrastructure (Farooq et al., 2019). For example, European Union (EU) member states aimed for a 10% renewable share in transportation fuel mix by 2020 (Al Jamri et al., 2020).

* Corresponding author at: Department of Agricultural and Biosystems Engineering, Makerere University, P.O. Box 7062, Kampala, Uganda.

E-mail address: nicholasmunu@yahoo.com (N. Munu).

The main advantage of liquid biofuels is renewability (Ogunkunle and Ahmed, 2019) since they are produced from versatile biomass feedstock such as agricultural crop residues (Ardebili and Khademalrasoul, 2018; Xue et al., 2017), energy crops, municipal waste (Karmee, 2016; Barampouti et al., 2019; Meng et al., 2019), forestry residues (Ballesteros and Manzanares, 2019; Nyström et al., 2019), wood processing residues (Kallio et al., 2018), algae (Kumar et al., 2020b; Pablo et al., 2020; Zhou and Hu, 2020; Kumar et al., 2018; Ashokkumar et al., 2017) and waste animal fats (Ardebili and Khademalrasoul, 2018; Toldrá-Reig et al., 2020; Riazi et al., 2020; Ndiaye et al., 2020). Liquid biofuels used in transportation fuel blends include pyrolysis bio-oils, bio-based alcohols (ethanol, butanol, isobutanol and isopropanol), and biodiesels (long-chain fatty acid alkyl esters from vegetable oils, animal fats/oils and waste cooking oil). Pyrolysis bio-oils are especially attractive because of ease of production and besides blending into transportation fuels they are also precursors for renewable chemicals and can be utilized in energy production through combustions and cogeneration and other industrial applications (Xiu and Shahbazi, 2012). Also, application of biochar from biomass pyrolysis into soil sequesters carbon (Criscuolo et al., 2014; Lehmann, 2007).

Lee et al. (2020) blended diesel, n-butanol, and coffee ground pyrolysis bio-oil and applied the blend in diesel engine electric generator. They found that NO_x and PM decreased by 15%–30% and 70%–90% respectively compared to neat diesel. Prasad and Murugavelh (Prasad and Murugavelh, 2020) blended tomato peel pyrolysis bio-oil with diesel and investigated the performance, combustion and emission characteristics of the resulting blend applied in a diesel engine. Fu et al. (2017) emulsified corn stalk pyrolysis bio-oil with diesel and $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ nanoadditive and tested in diesel engine. They found that a 20% bio-oil proportion showed reduction of specific fuel consumption of about 8.4% that of neat diesel and that increase in bio-oil content effectively decreased NO_x emission. Other studies on bio-oil/diesel blends from agricultural wastes include among others pyrolysis bio-oils from: rice husk (Prabhakar et al., 2020), walnut shell (Zhang et al., 2019), *Calophyllum Inophyllum* seed cake (Rajamohan and Kasimani, 2018), *Aegle marmelos* de-oiled cake (Baranitharan et al., 2019; Paramasivam et al., 2018), Coconut shell (Masimalai and Kuppusamy, 2015), *Prosopis Juliflora* (Masimalai and Kuppusamy, 2015), Mahua seed (Pradhan et al., 2017), *Jatropha Curcas* shell (Patel et al., 2018), and Neem seed (Alagu and Sundaram, 2018).

Pyrolysis is thermochemical breakdown of biomass in an oxygen-deprived atmosphere (Bridgwater, 2012; Jahirul et al., 2012). There are three main types of pyrolytic reactions differentiated by operating conditions: conventional/slow, fast and flash pyrolysis (Jahirul et al., 2012; Kan et al., 2016; Mohan et al., 2006). They differ in heating rate, operating temperature, feedstock particle size, and residence time (Jahirul et al., 2012; Mohan et al., 2006). Slow pyrolysis of agricultural waste to produce bio-oil is a viable green technology option that can fast-track adoption of green transportation in developing countries because it is relatively low-tech and requires little capital investment and can be easily down-scaled to suit splintered smallholders in these settings. Utilization of crop residues for production of second-generation biofuel energy can potentially curb greenhouse gas emissions, enhance energy security, and benefit local environments and rural economies without compromising land for food production (Xue et al., 2017; Zhao et al., 2015; Tilman et al., 2009; Adewuyi, 2020; Ayamga et al., 2015).

Corn is the largest grown crop in Sub-Saharan Africa (SSA) (OECD-FAO, 2015) and is a staple (Ayanlade and Radeny, 2020). Much work has been done to convert corn stover to bioethanol through saccharification and co-fermentation (Zhu et al., 2020; Liu et al., 2019; Qin et al., 2018; Zhang et al., 2010; Li et al.,

2010), however, adoption of this technology has lagged in developing countries. This is partly due to dominance of smallholder farming (Gollin, 2014; Morton, 2007) promoted by culture of land fragmentation in these settings which complicates large scale agricultural waste collection required for economically feasible bioethanol production through saccharification and co-fermentation. Communal land control, prevalent in these settings, also create bottleneck to largescale production of feedstock for biofuel production (Adewuyi, 2020). An appropriate technology that enables smallholders convert their agricultural waste to high-value bio-oil on individual or small-group scale will leverage smallholder contribution to global carbon footprint mitigation and act as local green technology to accelerate transition to green transportation in resource-limited settings. Consequently, improvement in energy supply and consumption will directly impact economic growth of these countries (Munu and Banadda, 2016).

In this paper we present a novel approach for the development of corn stover slow pyrolysis bio-oil/diesel blends that can be easily adopted by smallholders in developing countries. We emulsified corn stover pyrolysis bio-oil with neat diesel using Span 20 surfactant and discussed the relevant quality tests for their suitability as transportation fuel in diesel engines. The application of Span 20 emulsifier in corn stover bio-oil/diesel blends was not previously reported in open literature.

2. Materials and methods

2.1. Feedstock preparation and characterization

Corn stover samples were harvested from smallholder farms in Gayaza, Uganda and sun-dried for two days then size-reduced by chopping, crushing and milling. Fractions were homogenized and the mixture was subjected to sieve analysis for particle size distribution. Samples with mid-range of 12.5 mm were isolated for pyrolysis through particle range analysis. Properties of corn stover feedstock used in this study are shown in Table 1. Corn stover cellulose, hemicellulose and lignin contents were determined using NREL/TP-510–42618 standard method (Sluiter et al., 2008).

2.2. The pyrolysis system

Fig. 1 shows the pyrolysis system process scheme that was used to convert corn stover feedstock to bio-oil at Makerere University Agricultural Research Institute Kabanyolo. The equipment was conceived and designed by a research team at University of Kentucky Chemical Engineering Department as an appropriate technology for smallholders in developing countries. The pyrolysis system consists of four main parts: stove assembly, reactor assembly, piping works and a radiator acting as condenser.

2.3. Feedstock pyrolysis to produce bio-oil

The feedstock was loaded into an air-tight reactor to prevent oxygen admission and the system was fired. Reactor temperature was monitored with a probe connected to a digital display. Reactor temperature was gradually increased until the desired level of 350 °C after which temperature was maintained for one hour to bring the experimental run to an end. Feedstock thermally degraded in the reactor and released condensable and incondensable gases. Condensable gases condensed into liquid bio-oil while the incondensable gases exited the system as syngas. The experimental run was considered complete when no syngas exited outlet which was about 1 h 30 mins after start. Experimental runs were repeated in triplicate and the bio-oil and tar were collected. Biochar remaining inside the reactor was also collected after process completion.

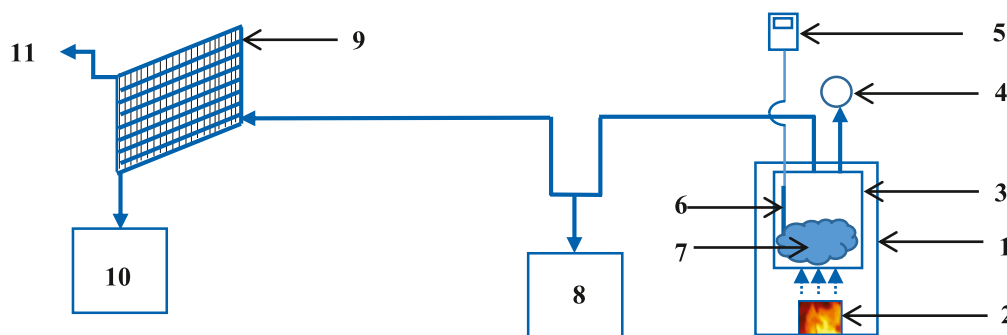


Fig. 1. Pyrolysis process scheme. 1: Stove assembly; 2: Furnace; 3: Reactor; 4: Pressure relief valve; 5: Digital Multimeter; 6: Temperature probe; 7: Feedstock; 8: Tar collection; 9: Radiator/Condenser; 10: Bio-oil collection point; 11: Syngas exit.

Table 1
Properties of corn stover feedstock.

Characteristics	Value
<i>Proximate analysis (wt %)</i>	
Moisture	12.5 ± 0.15
Volatile matter	66.2 ± 0.99
Fixed carbon	15.7 ± 0.47
Ash content	5.6 ± 1.22
<i>Ultimate analysis (dry wt %)</i>	
Carbon	34.91 ± 0.76
Hydrogen	6.22 ± 0.14
Nitrogen	0.56 ± 0.03
Sulfur	1.06 ± 0.12
Oxygen ^a	57.25 ± 1.03
<i>Atomic ratios</i>	
H/C molar ratio	2.123
O/C molar ratio	1.231
C/N molar ratio	38.407
<i>Chemical composition (wt%)</i>	
Cellulose	36.23 ± 1.73
Hemicellulose	25.47 ± 1.30
Lignin	21.83 ± 0.15

^aObtained by difference.

2.4. Bio-oil physical and chemical characterization

Bio-oil pH was determined using a digital pH meter, HI 2215 pH/ORP Meter, Hanna Instruments, United States of America. The bio-oil specific gravity at 15 °C was determined according to standard procedure ASTM D1298 (ASTM D1298-12b, 2017) and its chemical components were identified through GC-FID. The obtained chromatographs and retention times of the bio-oil and tar were correlated to NIST Mass Spectral Library. Bio-oil components were classified according to their boiling points into naphtha (B.P. <172 °C), kerosene (172 °C < B.P. <232 °C) and vacuum gas oil (B.P. > 232 °C) (Uçar and Karagöz, 2009).

2.5. Development of bio-oil/diesel blends and their distillates

Bio-oil and petroleum fuels are naturally immiscible (Jahirul et al., 2012). The bio-oil/diesel blends were produced in different ternary concentrations as shown in Table 2 by emulsifying petroleum diesel and pyrolysis bio-oil with sorbitan monolaurate (Span 20) acting as a surfactant to increase emulsion stability (Prakash et al., 2011). Surfactant concentration was maintained at 1% (w.t.) in all the blends. The emulsions were processed under high speed mechanical agitation at 60–65 °C (Chiaramonti et al., 2003). Power input during mechanical agitation was maintained at about 0.01375 kW h/L for all blends. The surfactant had hydrophilic lipophilic balance (HLB) number of 8.6, an acid value (mgKOH/g) of 2.3 and water content of 0.3%. Both the hydroxyl value and saponification value were in conformity with required

Table 2
Ternary compositions of bio-oil/diesel blends.

Emulsion	Composition (%w/w)		
	Span 20	Bio-oil	Petroleum diesel
B0	0.0	0.0	100.0
B5	1.0	5.0	94.0
B10	1.0	10.0	89.0
B20	1.0	20.0	79.0

standards. Emulsions B5 and B20 were distilled, and their distillates refrigerated at 4 °C and impurities decanted off. B5 and B20 distillates were further subjected to the same characterization processes like B5, B10 and B20. Neat diesel (B0) acted as control in this study.

2.6. Characterization of bio-oil/diesel blends and distillates

B5, B10, B20, B5-distillate (B5-D), and B20-distillate (B20-D) were characterized at Petroleum Laboratory of Uganda National Bureau of Standards according to required fuel standards for obtaining license by commercial fuel stations in Uganda. Fundamental properties such as pH, specific gravity at 20 °C, kinematic viscosity at 40 °C, corrosiveness, distillation characteristics, and cetane index were analyzed.

2.6.1. pH And specific gravity

Bio-oil/diesel blends and distillate pH were determined using a digital pH meter, HI 2215 pH/ORP Meter, Hanna Instruments, United States of America. Specific gravities of blends and distillates at 15 °C were determined according to standard procedure ASTM D1298 (ASTM D1298-12b, 2017) and corrected to a corresponding value at 20 °C using a Density Correction Table that conforms to ISO norms. Bio-oil sample, 100 mL, was transferred into a measuring cylinder and the cylinder and content brought to 15 °C. The hygrometer, ISO 649/BS 718, was lowered into the sample oil and the specific gravity was recorded after stabilization.

2.6.2. Kinematic viscosity

Kinematic viscosities of the blends and distillates were determined at 40 °C according to standard procedure ASTM D445 (ASTM D445-19a, 2019). For each blend or distillate, sample fuel was introduced into a clean BS/IP/SL Shortened Form Viscometer, Poulten Selfe & Lee Ltd until the viscometer bulb was half full. The viscometer and content was mounted into a constant temperature bath, Tamson Instruments, and equilibrium temperature of system brought to 40 °C. A mucus sucker was employed to draw sample through an orifice until it reached an upper mark on the viscometer. A stop clock was started and the time for sample fuel free fall between the viscometer upper and lower

marks recorded. The kinematic viscosity of the sample blend or distillate was calculated according to Eq. (1).

$$v = Ct \quad (1)$$

Where, v = kinematic viscosity, mm^2/s ; C = viscometer constant, mm^2/s^2 ; t = free falling time between viscometer upper and lower marks, s.

2.6.3. Distillation characteristics

Distillation characteristics of the blends and distillates were determined according to standard procedure ASTM D86 (ASTM D86-19, 2019). The distillation of samples was performed in HDA 620 Distillation Apparatus. For each sample, 100 mL of the blend or distillate was transferred into a D86 distillation flask equipped with an ASTM thermometer. The distillation flask and its content was loaded onto the distillation apparatus and heated gradually starting at 20% machine heating level and ramped at 5% level until 40% machine heating level was achieved (which is a distillation ratio of about 4–5 mL/min). Initial boiling point of the fuel was recorded by taking the temperature at which the first drop of distillate was observed. The final boiling point was recorded when all the sample had evaporated from the distillation flask. Distillation volumes recovered at 250 °C, 350 °C and 365 °C were recorded as well as the distillation temperatures at 10%, 20%, 30%, 40%, 50%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% distillation volume recoveries.

2.6.4. Calculated cetane index

Calculated cetane index was used instead of cetane number (Aleme and Barbeira, 2012). The calculated cetane index was determined according to standard procedure ASTM D4737 (ASTM D4737-10, 2016) by use of four variable equation shown in Eq. (2).

$$CI = 45.2 + 0.0892T_{10N} + (0.131 + 0.901B)T_{50N} + (0.0523 - 0.420B)T_{90N} + 0.00049(T_{10N}^2 - T_{90N}^2) + 107B + 60B^2 \quad (2)$$

Where, $T_{10N} = T_{10} - 215$, $T_{50N} = T_{50} - 260$, $T_{90N} = T_{90} - 310$, $B = [e^{-3.5(D-0.85)}] - 1$, D = specific gravity at 15 °C. T_{10} , T_{50} and T_{90} are temperature values in degree Celsius at 10%, 50% and 90% distillation volume recovery respectively.

2.6.5. Copper strip corrosion test

Corrosiveness test was performed on distillates B5-D and B20-D according to standard procedure for copper strip corrosion test ASTM D130 (ASTM D130-19, 2019). For each distillate, 30 mL sample fuel was transferred to a pressure vessel and a freshly polished copper strip was immersed into the vessel. The vessel and content was brought to a temperature of 50 °C and maintained at this temperature for 3 h. The strip was then removed and tested for corrosiveness by comparison with ASTM copper strip standards.

2.7. Data analysis

Obtained data of emulsion and distillate properties were compared with commercial diesel fuel standards set out in Ugandan and East African standards for automotive gas oil (UNBS, 2019). Reported values are means of two replications in accordance with rules and procedures of Petroleum Laboratory, Uganda National Bureau of Standards.

3. Results and discussion

3.1. Characterization of bio-oil

The bio-oil specific gravity at 15 °C of $1.0287 \pm 0.025 \text{ g/cc}$ and pH of 3.74 ± 0.03 are very similar to reported values in literature. Sadaka and Boateng (2009) found that bio-oil specific gravity normally varies in the range of 1.1–1.2 g/cc and pH of 2.8 to 4.0. Mullen et al. (2010) reported specific gravity of corn cob and corn stover fast pyrolysis bio-oils to be 1.1770 g/cc and 1.2451 g/cc respectively. In their study, Omulo et al. (2017) also reported that bio-oils from slow pyrolysis of banana fractions (leave, stem and peel) had specific gravity in the range of 1.06–1.11 g/cc . The pH of banana-fraction bio-oils reported by Omulo et al. (2017) are slightly higher (4.23 to 5.59) than that of our pyrolysis bio-oil. The difference could be due to variation in feedstock. The corn stover bio-oil had a dark color and a distinctive smoky smell, which is widely reported for pyrolytic bio-oils (Keleş et al., 2017; Zhang et al., 2013; Bridgwater, 2004).

Fig. 2 shows chromatographs for pyrolysis bio-oil and tar. Table 3 shows the main chemical compounds identified from GC-FID analysis of the bio-oil according to their groups and boiling point classes. Only chemical compounds with pico-areas (pA) greater than 0.4% were notable and thus reported for simplicity purposes. The 15 noted compounds accounted for 94% pA while unidentifiable compounds accounted for remaining 6% pA. Acetic acid is the main component of the bio-oil contributing 45.679% followed by Methyl-propyl-ketone (MPK) with 11.620%.

The bio-oil was dominated by naphtha fraction (77.445% pA) followed by kerosene fraction (9.729% pA). Naphtha fractions are unstable and flammable and their dominance suggests the applicability of corn stover bio-oil in transportation. The naphtha fraction consisted of C_2 , C_3 , C_5 and C_6 hydrocarbons while the kerosene fraction consisted of C_7 , C_8 and C_9 hydrocarbons. At 77.445%, the naphtha fraction of our bio-oil, produced at 350 °C, is distinguishably high compared to values reported by Uçar and Karagöz (2009) in pomegranate seed bio-oils produced at higher temperatures: 13.76% (400 °C) and 17.67% (500 °C).

Bio-oil compounds in the range of C_2 – C_9 is a mixture of gasoline (C_4 – C_{12}) and diesel (C_9 – C_{25}) fuel compounds (Pradhan et al., 2016). The C_5 – C_9 accounted for a significant portion (39.738%) of the bio-oil suggesting high presence of petroleum range fuel components in the pyrolysis bio-oil. All identified components were either aliphatic or aromatic hydrocarbons. Aliphatic and aromatic compounds have good flammability which make them useful in production of transportation fuels (Yorgun and Yıldız, 2015). Furfural is obtained from hemicellulose by acid catalyzed dehydration of 5-carbon sugars (pentoses) (Lü et al., 2017). Phenol derivatives such as 4-Ethyl-2-methoxyphenol, 2-Methoxy-4-vinylphenol, Benzyl alcohol, and Guaiacol are primarily derived from decomposition of lignin (Mohan et al., 2006; Vithanage et al., 2017). Their presence therefore confirms that lignin decomposition can take place at a low temperature of 350 °C. This finding supports lignin degradation temperature range of 280–500 °C mentioned by Mohan et al. (2006).

Oh et al. (2015) also found compounds acetic acid, furfural, 2-Methoxy-4-vinylphenol, and guaiacol in corn stover fast pyrolysis bio-oil while 19 other compounds differed from our reported compounds. The difference is expected to spring from the fact that Oh et al. (2015) applied fast pyrolysis and also ZnCl_2 impregnation pretreatment on feedstock prior to pyrolysis, despite similar reaction temperature (343 °C) to this study (350 °C). They also reported that bio-oil furfural and levoglucosan contents increased from 1.2 (wt%) to 37.8 (wt%) and 0 (wt%) to 25.4 (wt%) respectively when ZnCl_2 feedstock impregnation was applied. Zhang et al. (2019) confirmed the presence of acetic acid, furfural, guaiacol and 4-Ethyl-2-methoxyphenol compounds in walnut shell fast pyrolysis bio-oil.

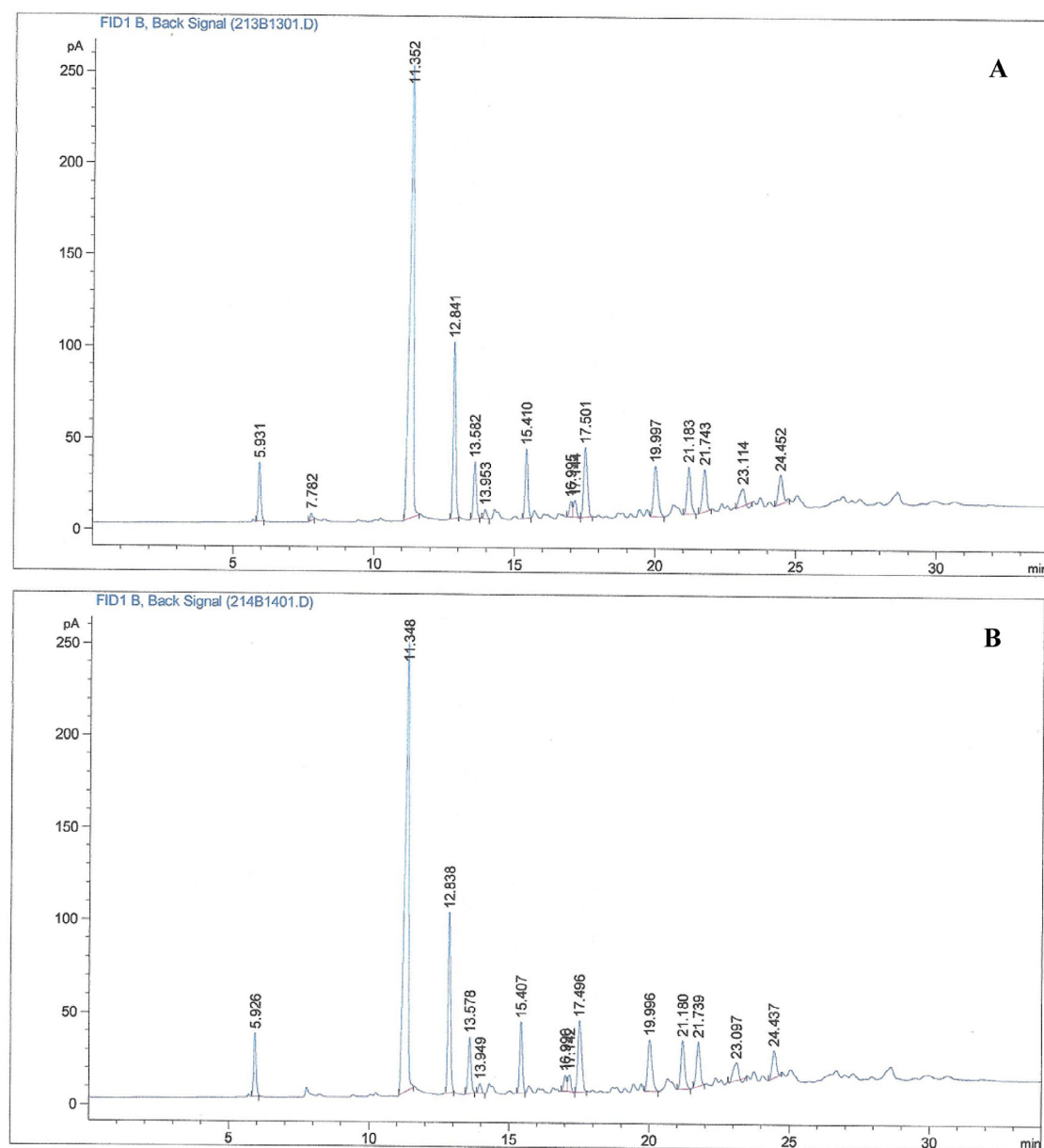


Fig. 2. GC-FID labeled chromatographs. (A) Bio-oil, (B) Tar.

Table 3

Main identified chemical fractions in corn stover bio-oil and tar.

R.T. ^a (min)	Compound	Chemical class	Molecular formula	Molar mass, (g/mol)	% Area	B.P. ^b , (°C)	B.P. Class
5.931	Acetaldehyde	Aldehyde	C ₂ H ₄ O	44.05	3.795	20.2	Naphtha
7.782	Ethanol	Alcohol	C ₂ H ₆ O	46.07	0.436	78.4	Naphtha
11.352	Acetic acid	Carboxylic Acid	CH ₃ COOH	60.05	45.679	118.1	Naphtha
12.841	Methyl-propyl-ketone	Ketone	C ₅ H ₁₀ O	86.13	11.620	101	Naphtha
13.582	Hydroxyacetone	Ketol	C ₃ H ₆ O ₂	74.08	4.267	145–6	Naphtha
15.410	3-Hexanone	Ketone	C ₆ H ₁₂ O	100.16	4.826	123	Naphtha
16.995	4-Ethyl-2-methoxyphenol	Phenol	C ₉ H ₁₂ O ₂	152.19	1.137	234–6	Vacuum gas oil
17.501	Furfural	Aldehyde	C ₅ H ₄ O ₂	96.09	6.822	161.7	Naphtha
19.997	2-Methoxy-4-vinylphenol	Phenol	C ₉ H ₁₀ O ₂	150.18	5.604	224	Kerosene
21.183	Octanol	Alcohol	C ₈ H ₁₈ O	130.23	4.526	195	Kerosene
23.114	Benzyl alcohol	Alcohol	C ₇ H ₈ O	108.14	1.857	205.3	Kerosene
24.452	Guaiacol	Phenol	C ₇ H ₈ O ₂	124.14	3.346	205	Kerosene

^aR.T. = Retention time.

^bB.P. = Boiling point.



Fig. 3. Bio-oil/diesel emulsions three months after production.

3.2. Properties of emulsions and their distillate

3.2.1. Stability of bio-oil/diesel blends

The color of the emulsions was off-white during production but changed to dark within 48 h. The blends were very stable with no phase separation witnessed three months after production, see Fig. 3. Proper production procedure by sequence, homogenization, methodology, and proportions of emulsion components contribute to stability (Chiaramonti et al., 2003). Homogenization breaks bio-oil into smaller droplets that are easily dispersed in the continuous oil (diesel) phase. The surfactant forms a layer around each bio-oil droplet with the lipophilic group oriented outward towards the continuous phase and the hydrophilic group oriented inward towards the bio-oil droplet. The lipophilic group creates a repulsion potential between the bio-oil droplets and prevents their flocculation and coalescence (Kumar et al., 2009). By this way the bio-oil droplets are prevented from coalescing in the continuous diesel phase.

Bio-oil concentration, surfactant concentration and power input per unit volume are factors that affect bio-oil/diesel emulsion stability (No, 2014; Ikura et al., 2003). The long-term stability of

all the emulsions (B5, B10, and B20) indicate that the applied 1 wt% surfactant concentration and 0.01375 kW h/L mechanical agitation power input were sufficient for all emulsion processing. This implies that lower concentrations of Span 20 surfactant such as 0.5 wt% and 0.1 wt% and lower mechanical agitation power input can be employed in future researches in an effort to optimize these variables and reduce processing costs. Whereas previous works have utilized Span 85 (Guo et al., 2014; Martin et al., 2014), Span 80 (Farooq et al., 2019; Guo et al., 2014; Wang et al., 2014), Span 60 (Martin et al., 2014), Tween 20 (Mulimani and Navindgi, 2018), Tween 60 (Farooq et al., 2019), Tween 80 (Guo et al., 2014), Tween 85 (Martin et al., 2014), and Hypermer B246SF (Ikura et al., 2003) at higher concentrations, this study confirms that Span 20 is not only a suitable surfactant for pyrolysis bio-oil/diesel emulsification but can be applied at much lower concentrations with non-negative implication on emulsion stability. Previous study with Span 20 surfactant in bio-oil/diesel emulsion involved producing a combination surfactant by mixing Span 20, Span 80, and Span 100 at ratio of 20 wt%, 20 wt%, and 60 wt%, respectively, and applying it to rice husk fast pyrolysis bio-oil and diesel emulsion (Lu et al., 2012). Farooq et al. (2019) reported that mixture of Span 80 and Tween 60 with HLB value of 7.3 conferred the most stable ether-extracted bio-oil/diesel emulsions that were stable (without phase separation) for 40 days and 35 days. This is well below the three months' stability reported in this study insinuating superiority of Span 20. Additionally, unlike Span 40 and Span 60 that have gel transition temperatures of 42 °C and 53 °C respectively, Span 20 with transition temperature of 16 °C averts gel formation at room temperature but remains liquid (Khoe and Yaghoobian, 2017).

3.2.2. B5-D and B20-D yields

Distillations of B5 and B20 resulted in 99% and 98% volume recoveries respectively. Impurities that were decanted off after distillation accounted for less than 1% v/v of the bio-oil/diesel blends. This implies that significant amounts of bio-oil were retained in the B5-D and B20-D samples. Fig. 4 shows yield and impurities from B20 distillation. B5-D and B20-D had deep-yellow appearance in contrast to dark color of B5 and B20. Visual comparison of B20, B20-D and diesel is shown in Fig. 5.

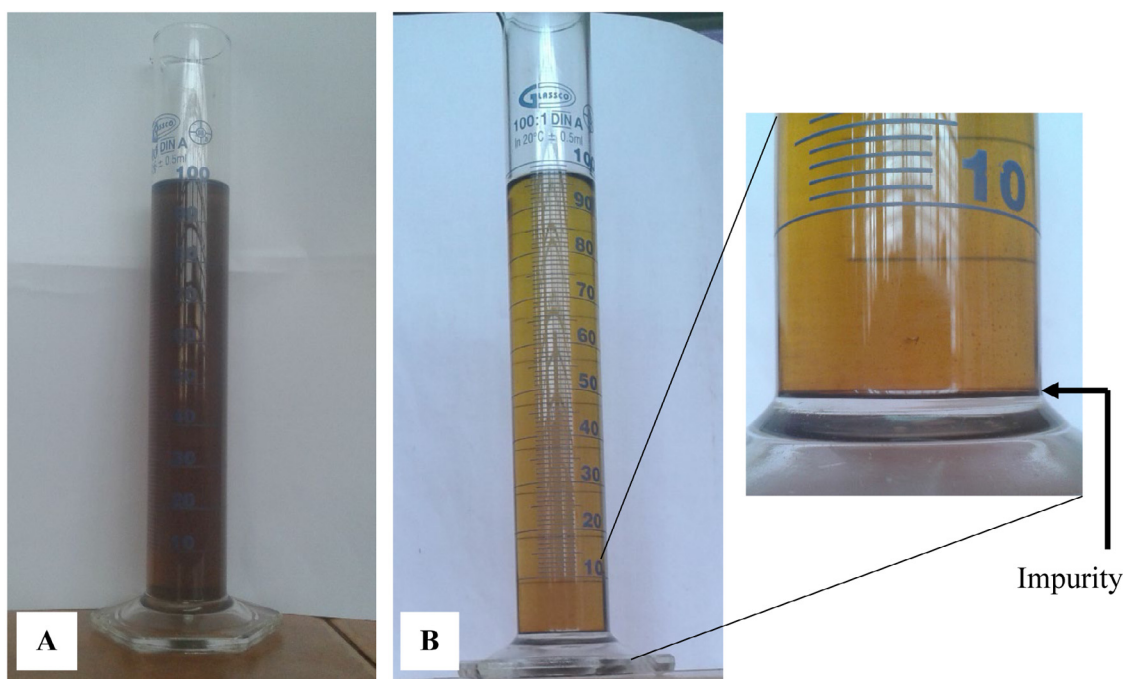


Fig. 4. Recovery yields of B20 distillation. (A) B20 before distillation. (B) B20-D before decanting.

Table 4
Properties of bio-oil/diesel emulsions in comparison to diesel standard.

Sample Id	Specific gravity at 20 °C, kg m ⁻³	Specific gravity at 15 °C, kg m ⁻³	Kinematic viscosity at 40 °C, mm ² /s	pH value	Copper strip corrosion (3h, 50 °C)
Diesel standard (UNBS, 2019)	817–867	820–870	2.0–5.3	– ^a	Class 1
B0	818.5	822.0	2.63	– ^b	
B5	825.8	829.3	3.20	3.47	
B10	826.2	829.7	3.21	3.45	
B20	827.2	830.7	3.22	3.42	
B5-D	823.9	827.4	3.01	– ^c	Class 1a
B20-D	825.1	828.6	3.09	– ^c	Class 1b

^aValue not defined.

^bThe pH meter could not give a reading on sample commercial diesel from station.

^cThe pH meter could not give reading on sample distillates.

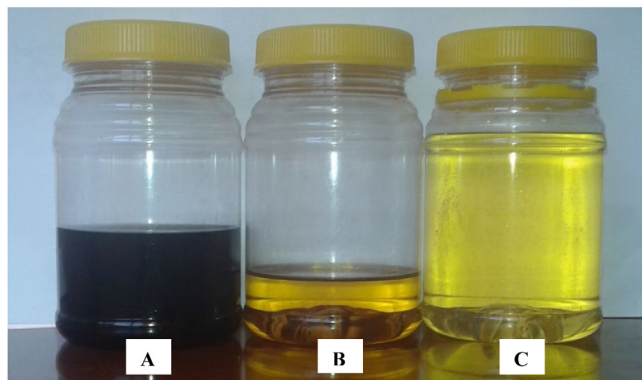


Fig. 5. Fuel color comparison. (A) B20, (B) B20-D, (C) Neat diesel (B0).

3.2.3. Specific gravity, kinematic viscosity, and pH

Table 4 is a comparison of B5, B10, B20, B5-D and B20-D pH, specific gravity, and kinematic viscosity to the required standards for automotive diesel in East Africa (UNBS, 2019). B5-D and B20-D corrosiveness are also shown. Emulsion specific gravities slightly increased with increase in bio-oil content. B5-D and B20-D had lower specific gravities than their original emulsions but the effect of bio-oil component was present in that B20-D had higher specific gravity than B5-D. Increase in emulsion bio-oil content increased kinematic viscosity (Pradhan et al., 2017; No, 2014). The neat diesel kinematic viscosity at 40 °C (2.63 mm²/s) is similar to value (2.58 mm²/s) reported by Pradhan et al. (2017). Emulsion pH were slightly lower than diesel pH (3.6–5.6) stated by Khan et al. (2013). Like neat diesel, distillate pH could not be detected by the pH meter used therefore their corrosiveness was tested by copper strip corrosion test. Specific gravities and kinematic viscosities of all the blends and distillates compare well with the required diesel standards. The blends are slightly acidic and may be corrosive but both distillates are within the required standards for corrosiveness. Result from copper corrosion tests suggest that B5-D and B20-D are suitable for application in diesel as transportation fuel (UNBS, 2019).

3.2.4. Distillation characteristics and cetane index

The distillation curve is an important parameter for gauging transportation fuel properties and performances (Hansen et al., 2020). Distillation curve is indicative of (1) fuel volatility (Hansen et al., 2020; Niculescu et al., 2019), which is affected by intermolecular interactions, and (2) fuel viscosity (Hansen et al., 2020). Fuel volatility has significant effect on spray penetration and mixture formation (Niculescu et al., 2019) and therefore studying distillation characteristics of fuels is highly regarded among fuel experts. Distillation characteristics of the emulsions and distillates are shown in Fig. 6. The initial boiling points

(IBPs) of B5, B10 and B20 were generally lower than that of diesel fuel but distillates B5-D and B20-D had similar IBPs to diesel. The distillation curves of emulsions and distillates showed similar shapes/trends to that of diesel fuel but for temperatures greater than 200 °C diesel fuel had a higher volume recovery than emulsions and distillates, about 10%v/v higher between 200 °C and 330 °C. This could be due to inferiority of neat diesel viscosity (2.63 mm²/s) compared to viscosities of emulsions (3.2–3.22 mm²/s) and emulsion distillates (3.01–3.09 mm²/s) or due to presence of compounds with higher boiling points in the pyrolysis bio-oil. In their study, Zschocke et al. (2017) reported that the distillation curves of Jet A-1 fuel shifted to higher temperatures upon mixing it with higher boiling point alternative fuels Farnesane and HVO (Hydrotreated Vegetable Oil). Similar findings are reported by Niculescu et al. (2019).

Corn stover pyrolysis bio-oil processed at 400 °C (similar to this study's 350 °C) contains 45.3% fraction (180–250 °C boiling point range) and 33.7% fraction (≤100 °C boiling point range) (Capunitan and Capareda, 2013). Bio-oil fraction with higher boiling point range (180–250 °C) than diesel fuel (IBP of 156 °C) could explain the shift in distillation curves of emulsions and emulsion distillates to higher temperatures (Zschocke et al., 2017). In this study, that fraction is composed of compounds 4-Ethyl-2-methoxyphenol, 2-Methoxy-4-vinylphenol, Octanol, Benzyl alcohol, and Guaiacol contributing about 16.47% of bio-oil composition as shown in Table 3. Bio-oil fraction with ≤125 °C boiling point range could explain IBP dip of B5, B10 and B20 from 156 °C (neat diesel) to 142 °C, 143 °C, and 140 °C respectively. Generally, it can be related that the higher the bio-oil content, the more the dip in IBP of the emulsion. Compounds with ≤125 °C boiling point range contributed 66.4% of bio-oil composition in Table 3 including Acetaldehyde, Ethanol, Acetic acid, Methyl-propyl-ketone, 3-Hexanone.

All the emulsions and distillates had final boiling points less than 370 °C, well below the required diesel standard of 400 °C (UNBS, 2019). The distillation characteristics of all the bio-oil/diesel emulsions and distillates compare well with required standards as shown in Table 5. The calculated cetane index for all the bio-oil/diesels emulsions and distillates were also within required diesel standards (UNBS, 2019). Although the IBPs of B5-D and B20-D were closer to that of conventional diesel, their distillation curves were closer to curves of the emulsions than that of the diesel fuel which confirms the presence of bio-oil compounds in the final distillates.

3.2.5. Useful observation during distillation of B5, B10, and B20

It was noted that distillations of bio-oil/diesel emulsions were accompanied by uneven temperature rise. Distillation temperature remained constant at 71 °C for about 40 min before increasing steadily. During the constant-temperature period, distillation process was accompanied with audible popping and shaking of the distillation flask. The delay, popping and shaking were absent with neat diesel fuel and distillates.

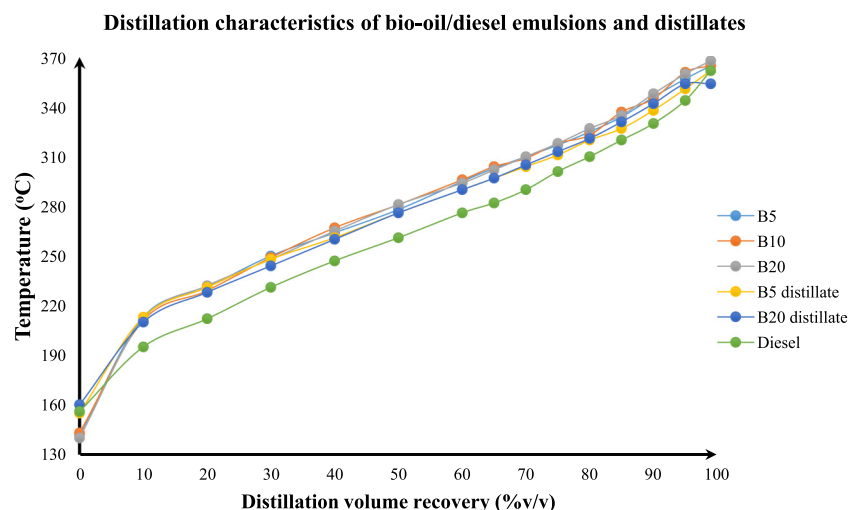


Fig. 6. Distillation characteristics of bio-oil/diesel emulsions and distillates.

Table 5
Distillation characteristics of bio-oil/diesel emulsions and distillates.

Characteristic	Diesel standard (UNBS, 2019)	B0 ^a	B5	B10	B20	B5-D	B20-D
Initial boiling point, °C	TBR ^b	156	142	143	140	155	160
250 °C recovery, (%v/v)	Max. 65	42	30	30	31	31	34
350 °C recovery, (%v/v)	Min. 85	96	92	92	90	94	93
365 °C recovery, (%v/v)	Min. 90	Fin. ^c	Fin.	97	97	Fin.	Fin.
95%v/v temperature, °C	Max. 360	344	357	361	360	351	354
Final boiling point, °C	Max. 400	362	365	365	368	362	354
Cetane Index	Min. 48.0	55.47	57.09	57.35	56.95	57.63	56.80

^aSample commercial diesel procured from fuel station.

^bTBR = To be reported.

^cFin. = Finished.

3.2.6. Implications of distillation characteristics and cetane index

Based on the distillation curves, the emulsions are suitable for application as transportation fuels. Their adoptions could be limited by three drawbacks: (1) dark color which is not appealing for application in engines, (2) high acidity, and (3) constant-temperature periods during distillation which might signal difficult cold starting. The distillates however do not have these limitations. There is improvement in color (Fig. 5), no constant-temperature periods during their distillation and are within required corrosiveness (Table 4). Distillate pH test results also showed similarity to conventional diesel fuel. With less than 1%v/v impurity removal after emulsion distillation coupled with uninterrupted heating characteristics, the distillates are better options as renewable fuels for application in diesel engines. This implies that one-pass simple distillation and impurity decantation can improve pyrolysis bio-oil/diesel blends quality for diesel engine applications. It is known that simple distillation improves neat bio-oil fuel quality (Biradar et al., 2014). The emulsions can be used in co-firing of boilers, thermal power plants, and furnaces (No, 2014; Hou et al., 2017, 2016).

The calculated cetane indices of all the emulsions and emulsion distillates were higher than for neat diesel probably due to the high presence of oxygenated compounds in bio-oil. The bio-oil is 36–37% oxygen by weight and all bio-oil compounds in Table 3 are oxygenated. High oxygen content improves cetane number but also lowers the energy contents of emulsions (Sivaramakrishnan and Ravikumar, 2012). Neat diesel is a pure hydrocarbon having zero oxygen content (Nadeem et al., 2006). Oxygen content of fossil oils vary in the range 0.05–1.5 wt% (Mohan et al., 2006). Neat diesel therefore presented the lowest cetane index compared to all the emulsions and distillates. However, due to zero oxygen content, combustion of diesel fuel is expected to

generate more energy than the emulsions and emulsion distillates. Sivaramakrishnan and Ravikumar (2012) performed a study on the cetane number of biodiesel blends made from different crops and found that they generally have higher cetane number than conventional diesels. This was also reported by other researchers (Uyumaz, 2020; Yesilyurt et al., 2020). Cetane number of bio-oil is negatively impacted by moisture content (Masimalai and Kuppasamy, 2015; Biradar et al., 2014).

3.2.7. Techno-economic analysis

Table 6 shows a techno-economic analysis for the bio-oil/diesel blend production process from one tonne of corn stover in the context of a smallholder farmer in Uganda. The analysis reveal that the process is financially feasible. Limitation of the analysis is on surfactant cost and distillation energy requirements that were not considered. Correct analysis requires that these should be considered under bulk conditions. Biochar generated from the process is traded while syngas trading can be optional based on the smallholder farmer's locality and infrastructure.

Future work should involve conducting energy balance of the complete distillate production process at small scale and upscale prototype levels and carrying out diesel engine performance and emission analysis.

4. Conclusions

In this work a novel approach for production of bio-oil/diesel emulsions from corn stover and relevant tests were discussed. Bio-oil/diesel emulsions in ternary concentrations 5%, 10% and 20% bio-oil weight were developed with 1% concentration of sorbitan monolaurate as an emulsifier. The emulsions with 5% and 20% bio-oil weight were distilled and the distillates subjected

Table 6
Techno-economic analysis for bio-oil/diesel blend production process.

	Quantity	Expected cost (\$)	Expected Revenue (\$)
Capital Investment			
Pyrolysis system	1	1,500	
Operation cost/tonne feedstock			
Corn stover		N/A	
Transport		4	
Size reduction energy	25 kW h	5	
Pyrolysis process/tonne feedstock			
Biomass energy/firewood fuel		50	
Pyrolysis yield/tonne feedstock			
Biochar (34%)	340 kg		510
Bio-oil (35%)	350 L		— ^a
Syngas	N/A		
Bio-oil/diesel blend production (B20 scenario)			
Diesel	1400 L	1,385	
Mechanical agitation energy	22 kW h	4.4	
Bio-oil/diesel blend, 98% recovery	1715 L		1,696
Surfactant		— ^b	
Distillation energy (for B20-D production)		— ^c	
Total (Costs, Variable)		1,448.4	2,206

^aAll bio-oil generated are blended.

^bTo be analyzed under bulk purchase scenario.

^cNeed proper distillation system for estimates.

to similar tests to the emulsions. Fundamental properties such as pH, specific gravity at 15 °C and 20 °C, kinematic viscosity at 40 °C, corrosiveness, distillation characteristics, and cetane index were analyzed and collated with required standards for automotive diesel in fuel stations of East Africa. The bio-oil/diesel emulsions and distillates had property ranges: specific gravities at 15 °C 827.4–830.7 kg m⁻³, specific gravities at 20 °C 823.9–827.2 kg m⁻³, kinematic viscosities 3.01–3.22 mm²/s, initial boiling points 140–160 °C, final boiling points 354–368 °C, and calculated cetane indices 56.80–57.63. The results show that the emulsions and distillates meet the required standards for automotive diesel in East Africa. Future work should involve conducting energy balance of the complete distillate production process at small scale and upscale prototype levels and carrying out diesel engine performance and emission analysis.

CRedit authorship contribution statement

Nicholas Munu: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization. **Noble Banadda:** Conceptualization, Resources, Validation, Supervision, Project administration, Funding acquisition, Writing - review & editing. **Nicholas Kiggundu:** Validation, Supervision, Writing - review & editing. **Ahamada Zziwa:** Writing - review & editing. **Isa Kabenge:** Writing - review & editing. **Jeffrey Seay:** Resources, Validation, Supervision, Writing - review & editing. **Robert Kambugu:** Writing - review & editing. **Joshua Wanyama:** Writing - review & editing. **Albrecht Schmidt:** Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Datasets related to this article can be found at <https://data.mendeley.com/datasets/h47tcy4gd5/1>, an open-source online data repository hosted at Mendeley Data (Munu et al., 2021).

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