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- [Multi-criteria assessment of biomass gasification-based hybrid energy systems in remote area. Shakirov et al.](#)
- [Effect of operating conditions on the hydrothermal valorisation of sewage sludge. Madikizela et.al.](#)
- [HVO's sustainability potential as a complementation for diesel and biodiesel blends in Brazil. Julio et al.](#)
- [Insight into the production of phenol from co-pyrolysis of cellulose and sodium borohydride. Gu et al.](#)
- [Catalytic pyrolysis of torrefied olive stone for production of potential petrochemical alternatives. Ganda et al.](#)
- [Evaluation of in-situ and ex-situ hybridization study in the optimised transesterification of waste and pure vegetable oils. Etim et al.](#)
- [Malic Acid Production by Aspergillus oryzae: The Immobilised Fungal Fermentation Route. Brink et al.](#)
- [Parametric Comparison of Biodiesel Transesterification Processes Using Non-Edible Feedstocks: Castor Bean and Jatropha Oils. Baioni e Silva et al.](#)
- [Biostimulation of anaerobic digested wastewater using magnetic nanoparticles and an external magnetic field for biogas enhancement.. Amo-Duodu et al.](#)



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



- [Production of biocoal from wastewater sludge and sugarcane bagasse using hydrothermal carbonization. Mkhwanazi et. al](#)
- [Optimization of Organic Loading Rate Using Bio-methane Potential Test. Dimakatso et al.](#)
- [Anaerobic co-digestion of sewage sludge with sugar wastewater for biomethane production using Optimal design. Adedeji et al.](#)
- [A Simulation Study of the Combined Process of Torrefaction and Gasification of Lignocellulose Biomass \(Bagasse\) for Syngas and Methanol Production. Fajimi et al.](#)
- [Experimental investigations on utilisation of ethanol-methanol \(M25E75\) blend as fuel in an automotive spark ignition engine. Nidhi et al.](#)
- [Impact of life cycle assessment for municipal plastic waste treatment in South Africa. Olagunju et al.](#)
- [Co-gasification of biomass and plastic waste: A mini Review. Mazhandu et al.](#)



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Optimization of Organic Loading Rate Using Bio-methane Potential Test Dimakatso Mohwele Yvonne Mampane¹, Anthony Njuguna Matheri^{1*}, Belaid Mohamed¹

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Abstract

This study investigated the validity of kinetic models in predicting maximum biogas yield with an increase in the organic loading rate (OLR) and retention time of Cellulose, Activated sludge and Brewery waste as the studied biomasses in mono and co-digestion environments. The modified Gompertz, Logistics and Richardson kinetic models were used to derive the kinetic parameters for assessing the effectiveness of the correlations brought about by the studied models for a cumulative hydraulic retention time of 60 days. Bio-methane potential (BMP) tests were performed on a Bioprocess control AMPTS II digestion system to obtain produced biogas data for the kinetic models to predict the production of biogas. The digestion process was studied at a Mesophilic temperature condition of 37 °C and a pH range of 6.5-7. The carbon/ nitrogen ratio of all the studied substrates appeared to be within the required range of 15-30, which proved their adequate ability to provide stability to the bacteria used in enhancing the anaerobic digestion process; Cellulose had a ratio of 30.00, brewery 21.607 and the sewage waste 15.569 respectively. Sewage and cellulose appeared to be capable of maximizing the bio-methane accumulation with being mono-digested whilst increasing the OLR in co-digested samples also appeared to be favoring the production process as a results of more nutrients being available for the microbes to feed on during the production process. All the studied models proved to be eligible to provide



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



better correlation of cumulative bio-methane production and showing that both types of digestion procedures can play a major role in enhancing production.

Keywords- Anaerobic digestion; biomass; bio-methane potential test, kinetic models, organic loading rate

Introduction

The rise in the developments of the economy has suddenly procured the need of the availability of more fossil fuel sources to yield electricity with which they tend to be getting used up on a fast basis than back in the days (Matheri *et al.*, 2018b). The recent severe decrease of the availability of fossil fuels, the instability of their prices together with the rapid increase in global environmental problems have raised concerns on how electricity should be produced for future generations (Karki *et al.*, 2005). The fossil fuel shortage issue has encouraged the development and the establishment of clean energy measures that can be used in inhibiting the risk of the decrease in the supply of electricity amongst households; the measures are namely: solar energy, waste to energy, hydropower and wind energy. According to Berndes *et al.* (2003), waste to energy techniques plays a vital role in the sustaining of the environment together with its resources and living organisms. Fossil fuels are nonrenewable resources that constitute to a change in the climate conditions when incinerated to produce electricity. The combustion of fossil fuels releases harmful greenhouse gases which depletes the ozone layer that acts as a protective shield for the earth from harmful sun rays (Matheri *et al.*, 2018b).

Waste to energy technologies are energy measures used in the production of electricity from solid municipal waste materials. These technologies make use of the circular economy whereby waste materials are not allowed to leave the production system but, instead they are recycled back into the production process in order to conserve the environment and to assists production industries to refrain from polluting the environment with their linear production processes. Population growth



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Cape Town, South Africa
13-15 December 2021



in cities has increased waste generation which have turned out to be difficult to control. According to Ngoben (2018), landfill sites in the Gauteng province in South Africa specifically in the Johannesburg city are already flooding with waste; this is as a result of failed control measures initiated by the state to educate people on the importance of engaging in the recycling and the reuse of waste materials. The report made by Girotto *et al.* (2015) showed that the organic fraction of municipal solid waste materials has a great impact in having the ability to be utilized in the production of bio-methane due to its high nutrient content, hence this measure was considered to be effective in controlling organic municipal waste through producing electricity.

Waste to energy technologies utilizes anaerobic systems to control waste generation. Anaerobic digestion process involves the breaking down of organic materials by microorganisms to produce renewable energy that is efficient and environmentally friendly, performed without the presence of oxygen and using anaerobic temperature conditions. The waste materials normally used in the production of bio-methane involves animal manure, human waste, plant waste, papers and food leftovers (Matheri *et al.*, 2018c). The organic waste materials for the process are usually retrieved from disposal sites in different shapes, hence reduction is required to reduce it into fine solid particles before it can be loaded into a digestion reactor vessel for anaerobic digestion. The waste is reduced to prevent delays in the digestion process, using drying ovens operated at high temperatures. Crushed waste has to be mixed with a fluid in the form of water to create a pulp in the digester, allowing inoculated bacteria inside the vessel to occupy a larger surface area to increase the occurrence of the digestion process. The digester vessel should be kept tightly closed to inhibit the presence of oxygen inside the vessel. The occurrence of oxygen in the vessel might lead to low production rates, an imbalance of the performance of the digester vessel or dysfunctionalities of the vessel (Botheju and Bakke, 2011).

According to (Matheri *et al.* 2018c), the biogas fuel produced is made up of carbon dioxide at a percentage of about 39%, methane at 60% and a balance of water vapor, hydrogen sulphide and other contaminant gases by volume. Produced biogas fuel from anaerobic digestion can be directly



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



used to operate gas engines. Biogas can be further processed to be used as a source of fuel for vehicles, constituting of about 99% of methane (Wellinger *et al.*, 2013). In ensuring the efficient production of bio-methane, the analysis of parameters as listed below needs to be assessed: the temperature which has to be kept under Mesophilic temperature conditions, the hydraulic retention time, pH, the organic loading rate and the Carbon/ Nitrogen ratio. The temperature is crucial for the establishment of stability, the reaction rates and the activity of micro-organisms during the production of bio-methane.

One major critical aspect that this research study aims at addressing is the issue of the increase in climate weather conditions as a result of linear production systems. Waste generated by such industries is not effectively monitored, hence the introduction of anaerobic digestion processes with which are not are also not convenient as result of being too costly due to some kinetic parameters of the process not being correctly monitored during the production process. This research project is aimed at assessing and utilizing a Bio-methane Potential Test (BMP) to estimate the digestibility of an organic substrate to obtain a maximum methane production rate under different organic loading rate conditions and using modelling to predict the production of biogas prior being initiated.

1. Materials and methods

1.1. Waste quantification

The study was conducted at the Process Energy Environmental and Technology Station (PEETS), a laboratory at the University of Johannesburg by the Doornfontein campus. The biomass studied in this research involved cellulose, brewery waste and activated sludge (sewage). The cellulose was bought at the Johannesburg CBD, brewery waste collected from the South African Brewery (SAB) at Pretoria, whilst the sewage waste was collected from the Daaspoort wastewater drains at Pretoria.



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Protective safety equipment such as lab coat, safety gloves, and nose marks were required to inhibit the occurrence of occupational hazards.

1.2. Substrate characterization

Characterization of the waste was established to ascertain composition. The samples were analyzed as per the standard method of APHA 1995 (Matheri *et al.*, 2018a) to classify waste based on their contents proximate and ultimate analysis also known as the elemental analysis. Ultimate analysis characterized the samples elemental compositions into Carbon, Nitrogen, Hydrogen and Sulphur (CHNS); whilst proximate analysis assessed the physical and chemical compositions of the waste materials and specifically focusing on the moisture content, the total solid concentrations and volatile solid concentrations and C/N ratio:

1.2.1. Ultimate analysis

The CHNS of the ultimate analysis were assessed per the ASTM E870 as described by (Matheri *et al.*, 2018c). A Flash 2000 CHNS-0 elemental analyzer fitted with an auto-sampler was used to obtain the CHNS elemental values of the substrate. The properties of the elemental analyzer were assessed as follows: Both the oxygen and the carrier helium gas with a pressure of 250 kPa, reference flow rate of 100 mL/min, carrier gas flow of about 140 mL/min whilst that of oxygen was at about 250 mL/min, oven column temperature at 65 °C, Furnace temperature at 950 °C, with tin capsules used as sample holders, the detector being a Thermal Conductivity Detector (TCD) and using a quartz reactor.

Biomass was weighed at 1 mg using a tin capsule and the sample placed on an auto sampler to attain the CHNS values, inserted with an electrolyte on a quartz reactor to be introduced into a reactor cell. A TDC operated at an oven column temperature of 65 °C was used to detect the weight values (in weight %) of the CHNS elements to which were displayed on the laboratory computer, through oxygen on the samples combusting the sample carrier gas.



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



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1.2.2. Proximate analysis

Physical composition were assessed using a furnace to determine the total concentrations, volatile concentrations and moisture content of the sample. The Carbon/ Nitrogen (C/N) ratio which is a vital stability factor for the bacteria was calculated using Equation 1 as stated below:

$$\frac{C}{N} = \frac{(F \times C_f) + (S \times C_s)}{(F \times N_f) + (S \times N_s)} \quad (1)$$

The total solid concentration was attained as per the dry matter of the biomass with evaporating all the liquid in an oven operated at 180 °C for 24 hours and determined according to Equation 2:

$$TSC(\text{weight } \%) = \frac{\text{Sample of dry weight}}{\text{Sample of wet weight}} \times 100 \quad (2)$$

And the moisture content attained from the loss of weight of the samples per the elimination of water on them. Equation 3 was then used to calculate the moisture content:

$$MC(\%) = \frac{M_{Wet} - M_{Dried}}{M_{Wet}} \times 100 \quad (3)$$

Where, M_{Wet} was the mass of sample before drying and M_{Dried} being the mass of the sample after drying.

The volatile content was assessed in a desiccator using the samples from the oven that assisted in determining the total concentration content of the biomass through initially being weighed and then fed into a furnace at an ignition temperature of 550 °C for about 1 and a half hours, then cooled to room temperature and weighed again. The attained weights were used in Equation 4 as shown to determine the amount of volatile solids:

$$VSC(\text{weight } \%) = \frac{\text{Sample of dry weight} - \text{Sample of wet weight}}{\text{Sample of dry weight}} \quad (4)$$



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



1.2.3. Analytical method and bio-methane potential test

The reactant waste materials were diluted with water to form a slurry before being tested to speed up the digestion period. Prior being fed into the digester, the feedstock waste materials were kept in a fridge at 4 °C to prevent getting them digested before the actual digestion process could be addressed. To regulate the pH level of the inoculum and substrate, Sodium hydroxide readily available from PEETS lab was inserted on the studied biomass samples whilst Nitrogen also obtained readily from the lab was used for purging oxygen from the digester vessel to establish the AD environment.

This digestion process was performed under batch conditions using a Bioprocess control AMPTS II that is made up of 500 ml digester feed-batch digesters (represented by laboratory glass bottle reactors), a gas collection unit, Carbon dioxide fixing unit and connected to a personal computer (software) to attain the results of the accumulation of biogas. The volatile solid waste composition were used to determine the substrate to inoculum ratio added on the digester bottles (about 400 ml of substrate to inoculum amount was added to the digester leaving 100 ml of gas space for the attainment of the biogas production results). Preparation of the inoculum was done by eliminate biogas present in the initial substrate by digesting it for 14 days. The dried biomass was mixed with water to create a slurry mixture that was homogenized using a blender in order to speed up the reaction. The slurry sample mixtures were loaded into the batch digesters using organic loading rate ratios of 2 and 3 (substrate to inoculum) and the waste materials also studied singularly as controls of the AD process results accumulation. A pH meter was inserted on the digester units on a daily basis to monitor the stability of the bacteria and the digestion process during the AD process, a pH value of about 7 had to be maintained throughout using about 8 g of Sodium Hydroxide and Sulphuric acid in a 100 ml of water.

A thermostatic bath was fed with water and the waste fed bio-digester vessels placed in it, whilst the carbon fixing bottles together with flow cells were connected to it. The digesters were flushed with Nitrogen prior initiating the digestion process to purge any composition of Oxygen that was



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



present in the vessel which hinders the activity of methanogens thus leading to the attainment of a reduced rate of the produced biogas; the purging process was mostly focused on retain an AD environment in the vessels. The AD process was operated at Mesophilic temperature conditions of 37 degrees Celsius and an agitation speed of 30 seconds ON/OFF. The sample were kept in the water bath for a Hydraulic retention time of about 60 days to ensure the complete digestion process of the biomass. The produced biogas was measured using a downward displacement method until the end of the retention time was established and the results automatically recorded by a Computer that was connected to the AMPTS II system.

1.2.4. Modelling of anaerobic digestion

In optimizing this study, the computational tools that were used to perform the simulation process was as follows: Microsoft excel, as well as modelling algorithms. The modelling algorithms involved the Modified Gompertz, Richardson and Logistic models (Matheri *et al.*, 2016b). The models required to predict the production of energy from biomass were incorporated to describe sustainability of the biogas production and control kinetic parameters for the effective accumulation of biogas.

1.2.5. Models validation

Validation and optimization of the kinetic parameters was conducted through chemical modelling to ensure comparability of the experimental data as to meet the objectives.

1.2.6. Models Performance Evaluation

The efficiency of the predicted amount of energy from biomass was ascertained using the coefficient of determination, sum of square error and mean square error.

2. Results and discussions

This investigation evaluated the use of the Gompertz, Logistic and Richardson kinetic models to predict the effectiveness of Cellulose, Brewery waste and Sewage, under different organic loading rates to retrieve bio-chemical kinetic parameters that determines the Bio-methane potentials in an



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Anaerobic Digestion (AD) process operated at a pH of 7 and an optimum Mesophilic temperature of 37 °C.

3.1.Characterization of the substrates

The substrate characterization of the AD operation was performed with accordance to the standard method of APHA 1995 (Matheri *et al.*, 2018b) in order to classify them with respect to the ultimate and proximate analysis. It is vital to maintain a good substrate characterization in order to ensure an effective prediction of Bio-methane potential and modelling on various substrates.

Table 1: Substrate characterization of the biomass

Substrates	Characteristic Parameter							
	Weight %							C/ N ratio
	C	H	N	S	TS	VS	MC	
Cellulose	41.54	5.57	1.35	0.00	45.35	94.96	37.18	30.00
Brewery waste	42.35	5.53	1.93	0.00	24.32	73.27	86.88	21.61
Sewage	47.64	6.66	3.06	1.17	62.82	31.57	54.65	15.57

Substrate characterization results as shown in Table 1 were obtained before the actual BMP tests were initiated using ultimate and proximate analysis as thoroughly addressed in the following subsection.

3.1.1. Ultimate analysis

3.1.1.1.Elemental analysis of substrates

Ultimate analysis also referred to as the Elemental analysis, was used to characterize the elemental composition of the substrates, with which Carbon, Nitrogen, Hydrogen and Sulphur were detected in the substrates except for Oxygen as shown in Table 1. Oxygen composition was neglected from



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



the digestion process as a result of it being purged before operation, since the AD process operates in its absentia for the accumulation of a maximum Bio-methane potential (Botheju & Bakke 2011). The elemental analysis is a vital factor in the establishment of the molecular formula of biomass, also assisting in the prediction of the digestive process inputs and outputs through the kinetic modelling and simulation of waste to energy technologies (Matheri *et al.*, 2018a).

Fig. 1 shows the CHNS composition of the biomass. The results conclude that the studied substrates were dominated by the carbon content with cellulose made of 41.54 wt%, brewery 42.35 wt% and sewage made of 47.64 wt%; the sewage substrates appeared to have more of the Carbon as compared to the other two studied substrates. All of the biomasses constituted of both the Hydrogen and the Nitrogen content. There was no Sulphur content detected in both the cellulose and the brewery waste, whilst partially detected in the sewage waste. According to (Matheri *et al.*, 2018a), the elemental analysis of a biodegradable substance is supposed to be dominated by the Carbon element, followed by Hydrogen, then Nitrogen and lastly, it needs to have the least amount of the Sulphur element.

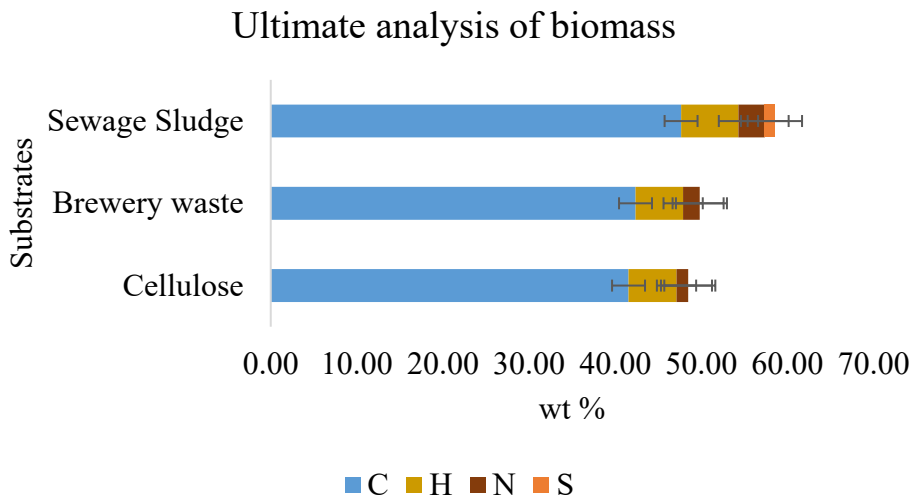


Fig. 1: The elemental analysis results of the substrates in weight percentages.



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



The high carbon content in all the studied substrates constituted to the necessary amount needed for maintaining growth of bacteria for enhancing the biogas production (Lin, 2012)

3.1.2. Proximate analysis

The elements distinguished by the elemental analysis in Table 1 were quantified the TS, VS, MC (in weight percentage) and used to determine the C/N ratio of the biomass.

The C/ N ratio was utilized as a factor for assessing the stability factor of the bacteria of the substrates (Abowei *et al.*, 2019), using equation 1 as shown in sub section 2.2:

Rabago (2014) explains that the C/ N ratio needed for the efficient production of biogas is within the range of 15-30. From Fig. 2, the C/ N ratio results of brewery, cellulose and sewage waste proved to have been eligible in providing enough stability for the micro-organisms responsible for digestion due to being within the required range with sewage made up of 15.569, brewery waste 21.607 and cellulose 30.00. According to (Arthur *et al.*, 2011; Matheri *et al.*, 2018a), a C/ N ratio greater than the optimum range results in an increased carbon content that yields more carbon dioxide during the digestion process which ultimately decreases the stability of the bacteria through lowering their pH value, thereby affecting the production of bio-ethane; a low C/ N ratio on the other hand refers to the availability of more Nitrogen content which results in the accumulation of Ammonia which increases the pH above 8.5 and inhibits the growth of bacteria thus reducing the rate of biogas production.



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



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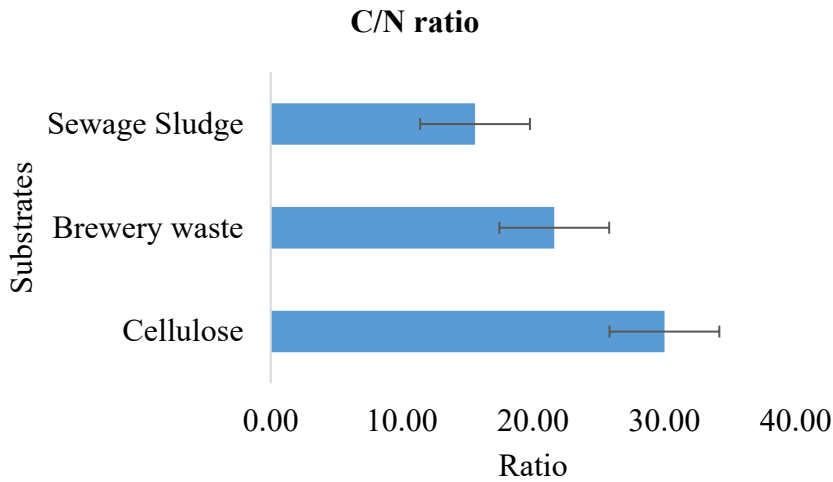


Fig. 2: The Carbon to Nitrogen ratio of the biomass or substrate.

The TS, MC and VS contents represented in Table 1 were calculated by the Excel application using Equation 2, 3 and 4 as shown sub section 2.2. The total solid concentration is the sum of the weight of dry and wet solids used to assess the efficiency of the digestion process, whilst the volatile solid concentration is the biodegradable total solids portion of the substrates (Matheri *et al.*, 2018b). The volatile solids for both the cellulose was within the weight percentage range of 80–90 showing that it was found rich in biodegradable solids necessary for the digestion process to yield biogas as compared to the brewery waste and the sewage, this results are supported by the study done by Amon *et al.* (2007) and that such substrates of this nature stands a greater chance to be utilized for thermo-chemical processes.



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Proximate analysis of the biomass

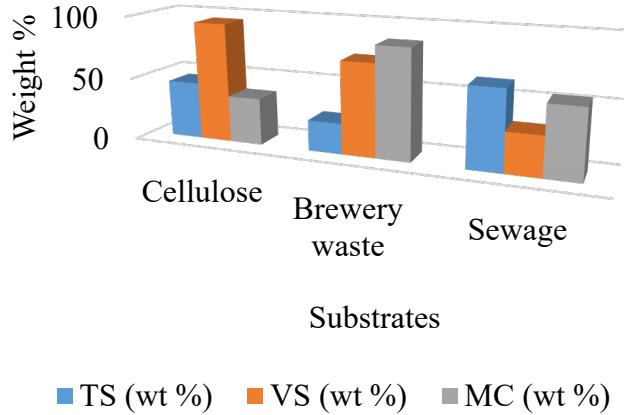


Fig. 3: Proximate analysis of the substrate.

Fig. 3 shows that cellulose was dry with a low moisture content of about 37.18 wt% whilst the other biomass samples showed to be immersed in water with the brewery waste at 86.88 wt% and the sewage waste at 54.65 wt%. These results showed that the brewery waste had enough moisture content for the fastest establishment of the AD as compared to the others.

3.2. Bio-methane potential test

The automatic methane potential test system (AMPTS II) was used to perform the AD bio-methane potential tests for the production of biogas using the mono and co-digestion of cellulose, sewage and brewery waste at an optimum Mesophilic temperature condition. As shown in Fig. 4, the BMP assay was conducted per day for a duration of 60 days to completely produce the biogas from the organic samples and the results obtained in Nml of methane/ g of the volatile solids. Rao *et al.* (2010), credits BMP tests for their reliability and validity in establishing a baseline for the performance of the AD process. Most of the analyzed samples showed characteristics that were quite similar to each other, with respect to the production of biogas especially in the first 14 days of the AD process. From the obtained results, there was no production of biogas from day 1 to 2



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



and this was as a result of the substrates being insoluble in the digestion process. A sudden rise in the production of bio-methane was observed during the initial 5 days of digestion for all the samples with which for the co-digestion samples, their production rate gradually decreased with the increase in the hydraulic retention time. According to Matheri (2018c), the increase in the production rate was as a result of agitation of the samples that assisted in the effective distribution of nutrients from the substrates to the microbes and the maintenance of an optimum temperature amongst the studied samples throughout the digestion process.

The sewage sludge mono digestion production led to the highest bio-methane accumulation at 1460.5 NmlCH₄/g VS as compared to the other mono digestion sample, with brewery waste at 185.9 NmlCH₄/g VS and cellulose at 1277.7 NmlCH₄/g VS. The brewery waste might have had a low production rate as result of the incineration process it went through with which happened to kill most of the microbes that were present in the organic matter. Fig. 4 results showed that there was a good production of bio-methane towards all the substrates that got to be co-digested with the sewage waste with that of sewage per the brewery waste at an OLR of 2 being 247.2 NmlCH₄/g VS whilst that at an OLR of 3 being 293.4 NmlCH₄/g VS and that the more the OLR gets increased, the more the production rate is established in the digester vessels.

The co-digestion of cellulose and brewery waste at different OLRs appeared to be less effective in the production of a maximum bio-methane potential; there was about 155.7 NmlCH₄/g VS amount of biogas produced at an OLR of 1: 2 of the cellulose to the brewery waste whilst there was about 170.7 NmlCH₄/g VS for an OLR 1: 3. The low production might have been as a result of the brewery intending to use up most of the sugar nutrients of the cellulose in order to initiate the digestion process since its' microbes lost their activity when the waste sample was incinerated. Fig. 4 present that the mono-digested samples had low HRT due to attainment of the optimum balance of the activity of microbes on their digestibility with which lowered the lag phase period since they took between 1 to approximately 20 days to reach maximum production rates, as compare to the co-digested samples. Overall, the AD production process under co-digestion of the



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



waste samples appeared to effective enough to initiate an optimum balance of microbes, creating a favorable digestive environments for them, thus enhancing the productivity rate of the biogas intended to be achieved.

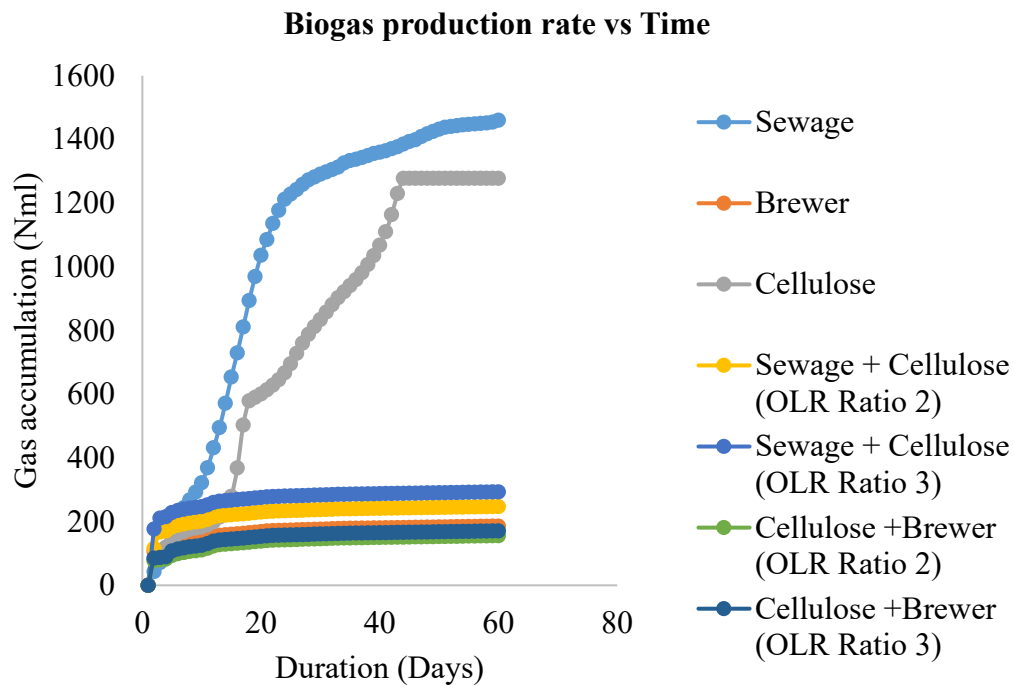


Fig. 4: Bio-methane potential test array from various mono and co digestion of biomasses

The results shown by Fig.4, indicates that the accumulation of biogas occurs and increases with the increase in the number of days that the digestion process is considered for.

3.3. Modelling of the bio-methane production

Primary modelling techniques were used as a factor for determining the kinetic parameters theoretically necessary to establish and analyze the establishment of a maximum bio-methane potential prior initiating the AD process, and to assists in limiting the over usage of resources during the production process. In this study, the mono and co-digestion of sewage, brewery and



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



cellulose organic waste materials were evaluated using the Modified Gompertz, Logistic and the Richardson kinetic models to fit a cumulative 60 day bio-methane production laboratory scale data of the biomass samples assessed at Mesophilic temperature of 37°C and a pH of 7; analyzed at different organic loading rates using non-linear regression as indicated by Fig. 5-10 to predict the production of bio-methane. Kinetic parameters were determined using the models, with the likes of the kinetic constant A (in ml/g COD) of the bio-methane potential, μ (in ml/g COD. day) for the maximum biogas production rate, λ (in days) as the lag phase period variable and R^2 for the coefficient of determination (Komilis *et al.*, 2017; Meego *et al.*, 2018); predicted using the non-linear regression approach for the best fittings using the goal seeking approach by the models in Microsoft excel to retrieve data as indicated by Table 2 and 3 respectively.

3.3.1 Mono-digestion modelling

The assessed models yielded the kinetic parameters as represented on Table 2 through mono-digesting the studied organic matters.

Table 2: The mono-digestion predicted modelled kinetic parameters

	Substrates	Kinetic parameters			
		A(ml)	$\mu(d^{-1})$	λ	R^2
Modified Gompertz	Sewage	1460	70.0041	5.52	0.8175
	Cellulose	1295	62	10	0.8799
	Brewery	185	8	0.01	0.7737
Modified Logistics	Sewage	1453	58	4.3667	0.8459
	Cellulose	1268	50	11.5	0.8744
	Brewery	183.5	7.0083	0.001	0.7976
Modified Richardson	Sewage	1465	700.9501	10.9398	0.9704
	Cellulose	1299	797.987	14.587	0.9506



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



	Brewery	188	120	0.01	0.7783
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In evaluating the kinetics of the prediction of the production of biogas, it was observed that sewage sludge contributed a large bio-methane potential in all the models as compared to the other organic waste sample. The modified Gompertz model gave about 1460 ml/g VS of bio-methane with Cellulose following by about 1295 ml/g VS and Brewery yielding the least amount at about 185 ml/g VS; the logistics model also yielded a greater amount of the sewage with about 1453 ml/g VS of bio-methane, with cellulose following by about 1268 ml/g VS and brewery yielding the least amount of bio-methane that was about 183.5; furthermore, the trend of the results remained the same in that sewage yielded about 1465 ml/g VS of bio-methane whilst cellulose followed by a out 129 ml/g VS and lastly brewery when modelling the results with the Richardson model. Sewage sludge had the highest production rate of methane as a results of its high nutrient content as compared to the other studied samples, cellulose followed with a greater production rate due to its high sugary content which appears to be the most necessity of maintaining the activity level of microbes. It was observed that the lag phase values for the sewage and the brewery waste was less than that of the cellulose, this shows that the production rate of the samples was to occur at a within a short retention time. The coefficient of determination for all the organic samples appeared to be within the required range of 0.8-1.0.

The cumulative biogas mono-digested produced results were modelled to fit in a curve using non-linear regression as indicated by Fig. 5-7:

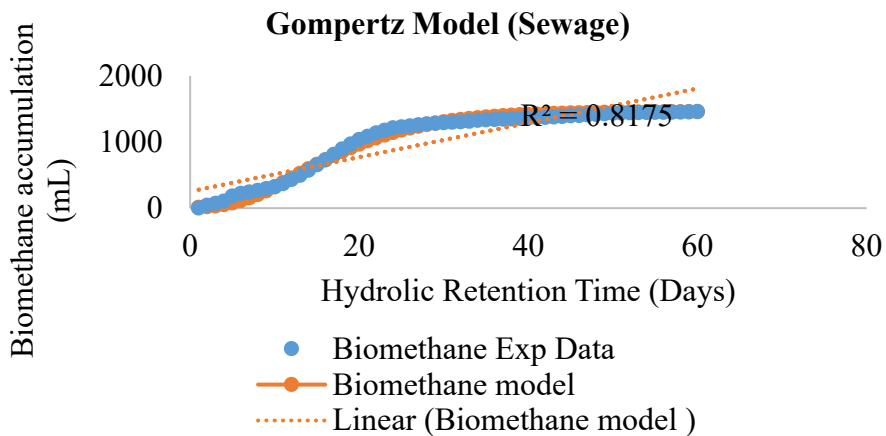


Fig. 5: Biogas accumulation prediction using Modified Gompertz model for sewage waste versus time.

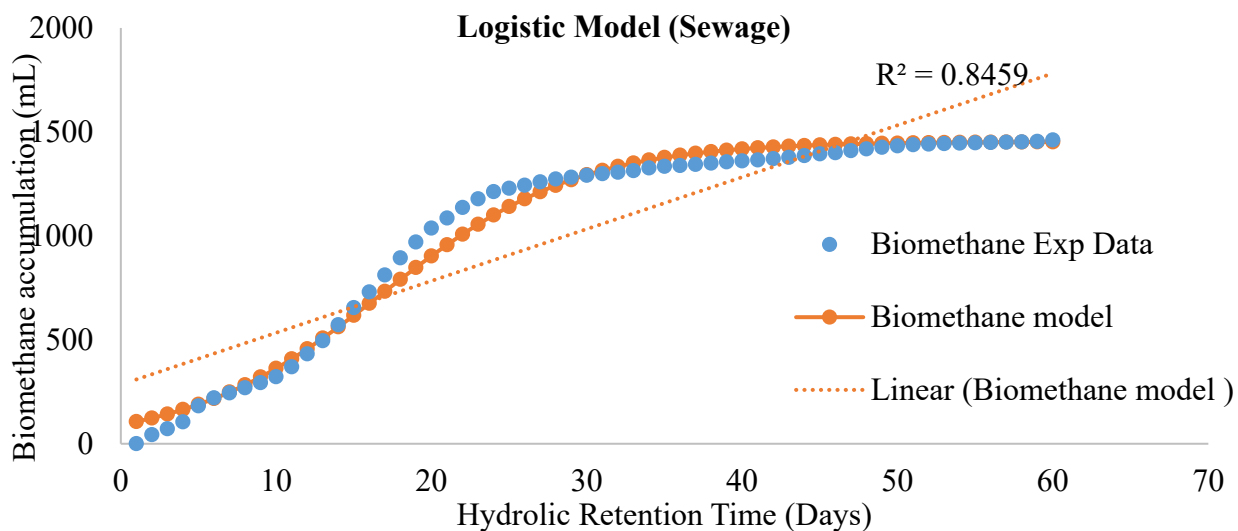


Fig. 6: Biogas accumulation prediction using Modified Logistic model for sewage waste versus time.



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Richards Model (Sewage)

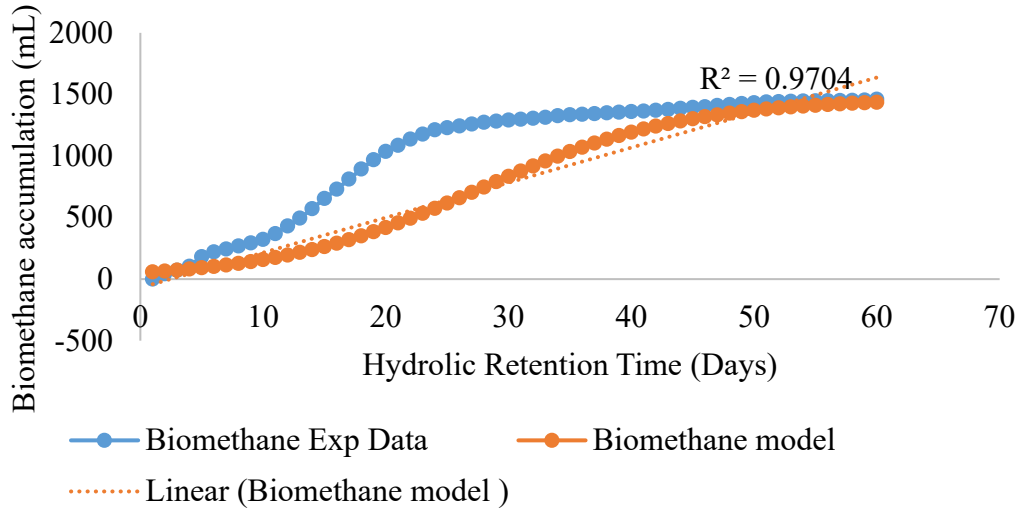


Fig. 7: Biogas accumulation prediction using Modified Richards model for sewage waste versus time.

From Fig. 5-7 above, it appears that the production rate of bio-methane increased with the hydraulic retention time between day 10-20 and this is because the time elapse, the more the activity of microbes becomes established hence the increase in the conversion rate; the conversion rate increased with the increase in time. Agitating the samples assisted in increasing the temperature in the digester vessels, with which played a vital role in ensuring an increase in the digestion rate of the waste materials to bio-methane.

3.3.2. Co-digestion modelling

Table 3 shows the co-digestion done on the prior mono-digested samples at OLR of inoculum to substrate of 1:2 and 1:3.



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Table 3: Kinetic modelling of co-digested biomass.

	Substrates	Kinetic parameters			
		A	μ	λ	R^2
Modified Gompertz	Sewage+ Cellulose (OLR 2)	248	8.7852	2	0.8715
	Sewage+ Cellulose (OLR 3)	298	15	12	0.8901
	Cellulose+ Brewery (OLR 2)	162	5	9	0.9589
	Cellulose+ Brewery (OLR 3)	170	9.9996	8.5705	0.8033
Modified Logistics	Sewage+ Cellulose (OLR 2)	248	8.6542	0.001	0.8459
	Sewage+ Cellulose (OLR 3)	292. 6852	8.4875	4.56	0.9442
	Cellulose+ Brewery (OLR 2)	156	8.961	18	0.9053
	Cellulose+ Brewery (OLR 3)	169	5.9710	3.5873	0.8785
Modified Richardson	Sewage+ Cellulose (OLR 2)	248. 58	150.06	0.00095	0.7934
	Sewage+ Cellulose (OLR 3)	290. 85	148	10	0.9589
	Cellulose+ Brewery (OLR 2)	154	126.9660	15	0.9035
	Cellulose+ Brewery (OLR 3)	170	99.6709	8	0.916

From Table 3, the accumulated bio-methane gas increases with the increase in the organic loading rate of the organic waste materials, this is because the microbes have enough nutrients to keep them active. Assessing all the models, it appears an increase in the OLR results in the occurrence of a reduced production rate of bio-methane, this is as a result of more substrates being in need of an inoculum to digest it into the intended biogas product. The kinetic model prediction results of



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



the lag phase for the co-digestion between sewage and cellulose shows that the increase in the OLR increase the retention time that the substrates needs to be digested by the inoculum. The coefficient of determination for the co-digestion modelling appeared to be within the required range of 0.8-1.0.

From the modified Gompertz model, the analysis made on the effect of the increase in the OLR (with the Sewage taken as the substrate and the Cellulose as the inoculum), predicted that the more the amount of inoculum on the digester, the more the produced biogas. At an OLR of 1:2 of the biomasses, the modified Gompertz model predicted to be eligible in producing about 248 ml/g.VS of biogas which appeared to be quite less than that of the sample studied at an OLR of 1:3 which yielded to about 298 ml/g.VS of biogas potential. The increase in the OLR of the biomass samples had a positive impact towards increasing the production rate of biogas, this was shown by the production rate of the 1:3 OLR sample being greater than that of the 1:2 OLR sample through having about 15 ml/g.VS.day as compared to the 1:2 OLR sample at 8.7852 ml/g.VS.day, thus showing that there was enough energy to from the microbes to facilitate the digestion process. The lag phase period was shorter for the 1:2 OLR sample as compared to that of the 1:3 OLR sample (presented by fig.8-9), taking about 2 days to reach maximum production than the 1:3 OLR sample with about 12 days, this is because the 1:3 OLR sample has more content to be digested as compared to the sample at 1:2 with less content in it with which contradicts with general analysis that the higher the OLR the shorter the lag phase period had to be achieved. The same trend of results of the predicted kinetic parameters were observed for the Cellulose and brewery waste co-digestion.

The co-digestion modelling conducted using the modified logistics model showed that the increase in the organic loading rate decreases the production rate of biogas instead of increasing it just like on the cellulose and brewery waste samples, this is shown by the results obtained for the 1:2 OLR sample of the sewage to cellulose sample with 8.6542 ml/ g.VS.day being greater than that of 1:3 sample at 8.4875 ml/ g.VS.day sample. The lag phase period for the 1:2 OLR sample appeared to



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



be shorter than that of the 1:3 OLR sample, this might be as a result of the nutrient content of the biomass content in the 1:3 sample being in large quantities; the less the lag phase period value the less time will be required for the digestion period to reach the optimum as shown in Table 3. The coefficient of determination for all the studied samples on the logistics model occurred to be within the expected range of 0.8-1.0, hence proved the Logistic model to be reliable for to fit a non-linear regression curve with effective results from the biogas accumulation data.

The amount of accumulated biogas increased with an increase in the OLR for both co-digestions using the Richardson model; for the sewage: brewery sample, when the OLR was 1:3 the amount of produced biogas was about 290.85 ml/g.VS.day as compared to the OLR at 1:2 at the value of 248.58 ml/g.VS.day, whilst the brewery waste occurred to produce about 170 ml/g.VS.day of biogas for the 1:3 OLR and about 154 ml/g.VS.day. The conversion of the biomass content to biogas increased with an increase in time, until reaching an equilibrium state after forming products, with the increase in the OLR of the organic contents. The lag phase values showed that the co-digestion of the cellulose with brewery waste had a higher lag phase period as compared to that of the sewage and the cellulose, this is because of the higher nutrient content that both sewage and the cellulose consists of and with which are vital for the maintains of the high activity of microbes during the digestion period. Keeping the digestion temperature within Mesophilic conditions assisted in dissociating the reactant particles to yield new products that involved an excess methane production with the co-digestion as the OLR was increased. The coefficient of determination occurred to be within the expected range of 0.8-1 for all the co-digested samples.

Fig. 8-10 shows the sewage to cellulose co-digestion as per the modeling of the Gompertz, logistic and Richardson methods.

Gompertz Model (Sewage+Cellulose, OLR 2)

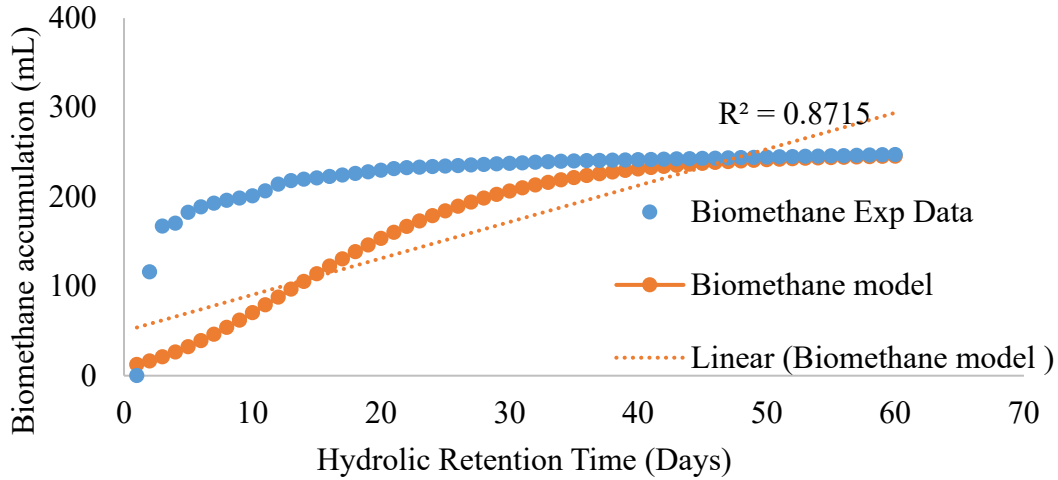


Fig. 8: The modified Gompertz co-digestion of sewage and cellulose.

Logistic Model (Sewage+Cellulose, OLR 2)

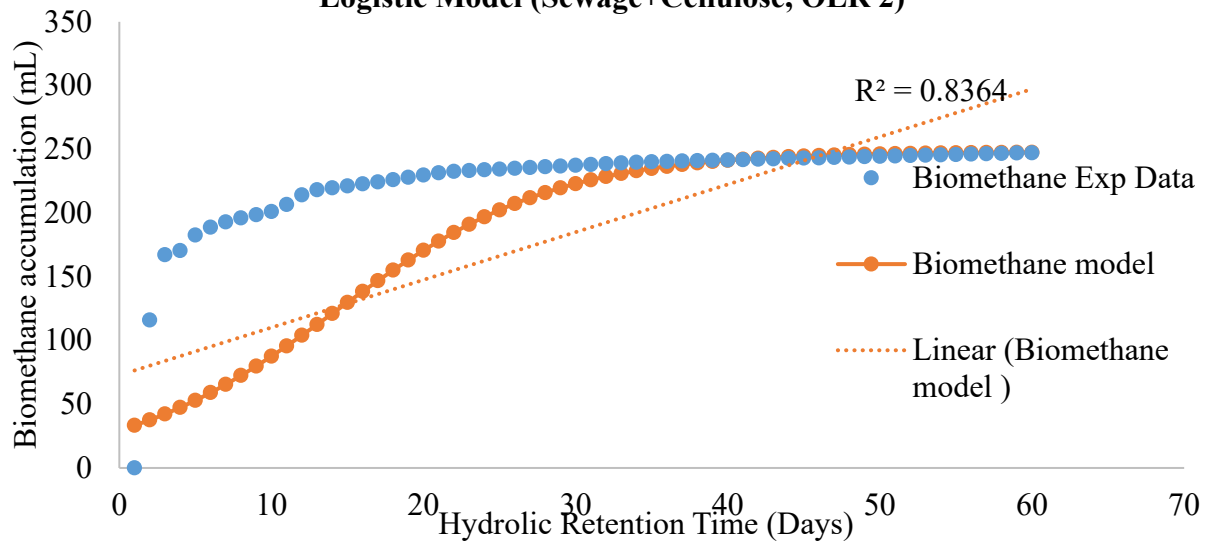


Fig. 9: Co-digestion of sewage and cellulose using the modified Logistics model.



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



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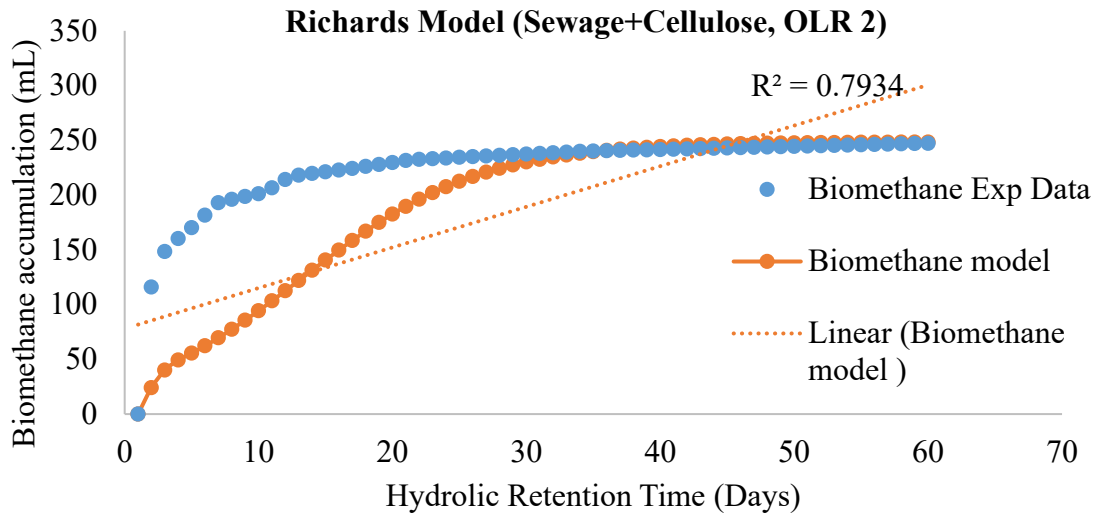


Fig. 10: The Modified Richardson’s modelled co-digestion of sewage and cellulose.

4. Conclusion

The application of the usage of the modified Gompertz, logistics and the Richards models appeared to be effective in predicting the results to be expected with the production of biogas in an AD environment prior being initiated with respect to the mono and co-digestion of the samples through increasing the hydraulic retention time and the organic loading rate of the biomass contents. An increase in the OLR appeared to be eligible in increasing the production rate, the accumulated biogas amount and establishing a short lag phase period for the production process as a result of more nutrient content being available for the microbes to feed on. The models also managed to produce perfect fits for the non-linear regression approaches with a coefficient of determination that was within the required range of 0.8-1.

5. Acknowledgement

The author wish to sincerely pass their deepest gratitude to the Process Energy Environmental and Technology Station (PEETS) at the University of Johannesburg, Doornfontein campus for access



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



to their laboratory where the BMP tests were performed and the Department of Chemical Engineering for sponsoring with funds for the biomasses.

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1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



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Cape Town, South Africa
13-15 December 2021



Anaerobic co-digestion of sewage sludge with sugar wastewater for biomethane production using Optimal design

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Keywords: Anaerobic co-digestion, sewage sludge, sugar wastewater, optimal combined design

Abstract

The use of sugar wastewater (SW) as co-substrate for the digestion of sewage sludge (SS) was investigated in this study as the use of food and agricultural wastes have been reported in past studies. The effect of varying the mix-ratio of the substrates, as well as that of temperature on the yield of biomethane (mL CH₄ g COD_t⁻¹) was evaluated to determine the optimum condition. An



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



optimal combined design (OCD) and numerical optimization tool were used in setting up the design and optimization of the associated variables. With desirability of 84.7%, the optimum condition for the co-digestion study was 2.3:1 for SS: SW and 28.7°C for a biomethane yield of 156.96 mL CH₄ g COD_i⁻¹. Results obtained reveals that the addition of SW aids in increasing the yield of biomethane, and the selected statistical tool could help in the prediction of the optimum conditions for the anaerobic co-digestion process.

Introduction

The desire for a sustainable environmental and renewable source of energy is a global phenomenon, with increasing compliance for a cleaner environment and energy. In recent decades, the conversion of waste into a source of renewable energy via anaerobic digestion (AD) has gained traction as an alternative means. ¹ The AD process uses microorganisms to convert carbon components into biogas (CO₂, CH₄, H₂, and slightly H₂S) by utilising the organic content of any substrate. ² However, the full application of the AD technique had been hampered due to some drawbacks in the digestion of a single substrate. Anaerobic co-digestion (AcoD), which involves the use of two or more complementary substrates, is a recent enhancement technique that has seen tremendous growth for alleviating the drawbacks of AD.³⁻⁵

In the last decade, various co-substrates such as food waste, algae, or sludge from industrial activities have been used. ⁶⁻¹² Recent research has found that using wastewater from agro-based



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



industries as a co-substratum to sewage sludge (SS) can boost biogas production. Wastewater streams from industries like winery-distillery, piggery slaughterhouse, and brewery have been used as SS co-substrates with interesting results.^{7,13-15} According to the literature, a few uses of food processing industry wastewaters include dairy, sugar, brewery, and slaughterhouse.¹⁶⁻¹⁸ It has been reported that wastewater from these industries has a high chemical oxygen demand (COD), which could serve as a substrate for microorganisms in the production of biomethane. According to Ripoll et al., while the production of methane was increased when sherry-wine distillery wastewater (SW-DW) was used as a co-substrate for SS, COD was also reduced by managing both wastes.¹⁵ Similarly, because the latter is in liquid form, the inherent nutrients will be soluble and will aid in providing adequate moisture for the AD or AcoD process.

As a result, the focus of this research is on the use of wastewater from the food processing industry, specifically sugar, as a co-substrate for SS. The substrate mix-ratios (SS and sugar wastewater (SW)) were varied to achieve the optimum mix for enhanced biomethane production. Since the mix of these substrates has not been reported in the literature, a varying mix ratio of the substrates is studied to determine the effect of changing substrate ratio based on volume (v/v). Because temperature has been shown to be directly proportional to the rate of methane production in the AD process¹⁹, the use of ambient, mesophilic, and thermophilic temperatures was considered in this study.



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



A mathematical model has been used in the prediction of AD and AcoD processes, either as a rate-determining step or to gain a better understanding of the system for scale-up purposes. Xie et al. reported that there are approximately five types of mathematical models for AD processes: kinetics, statistical, computation fluid dynamics, algorithm base, and anaerobic digestion model (ADM1).²⁰ The statistical model, which is a qualitative approach, is said to aid in the determination of optimum output through the design of input parameters and conditions. Most experimenters use statistical software for experimental design and optimization, such as Design Expert® from Statease, Minitab®, and JMP®.²¹⁻²⁴ In this study, Design Expert (version 13) was used to evaluate the effect of substrate mix-ratio on biomethane production and COD reduction, as well as to determine the optimum condition for biomethane production using the optimum combined design (OCD) in batch mode.

Materials and Methods

The SS used in this experiment was obtained from the Amanzimtoti wastewater treatment plant (KZN, SA). The samples were collected immediately after the primary settling tank, and their temperature and pH were measured on-site using a pH metre with a temperature sensor (Ohaus Corporation, USA). As the inoculum, anaerobic digested sludge from an existing anaerobic digester at the same wastewater treatment plant was used. The plant's digester was set to 25°C, and the pH of the inoculum was 7.19 at the time of sampling.



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



The sugar wastewater came from a sugar mill in KwaZulu-Natal, South Africa. Before any treatment was carried out, samples were taken from the effluent section. On the same day, the samples were also tested for total solids (TS) and volatile solids (VS) before being stored in the research laboratory's cold room at 4°C. Before and after the experimental runs, the VS and COD of the substrates mix and biodegraded samples were measured. Since 3M of NaOH(aq) was used for adsorption of any CO₂ produced, gas samples were measured once a week.

Analytical methods

Table 1 displays the pH, TS, VS, and COD of the substrates and inoculum. The analysis was carried out in accordance with the APHA's standard procedures.²⁵ The closed reflux method standard 5530D was used to determine COD. A 10 mL aliquot of SW or SS was filtered through a 0.45-micron syringe filter, then a 2.5 mL aliquot of filtered sample was poured into COD vials (HACH 2125925), digested for 2 hours at 150°C using the HACH COD block heater, and analysed with the HACH DR3900 spectrophotometer. COD concentration was measured using the COD high range (HR) stored programme 435 in the 0 – 1,500 mg/L range. A Gas Chromatograph (Shimadzu GC-2014, Shimadzu SA. (Pty) Limited fitted with a thermal conductivity detector (TCD) and a Porapak Q (80/100 mesh) packed stainless steel column with dimensions of 6 ft x 1/8 in x 2.1 mm was used to determine the composition of the gas produced. The column, oven, and detector were set to operate at 40°C, 120°C, and 250°C, respectively. Both the left and right column flows were kept at 20 mL/min, and the pressures were kept at 0.6 – 1.3 and 101.3 – 106.5 kPa on



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



both sides of the oven. Nitrogen gas was used as the carrier gas and various standard calibration curves were constructed for H₂, CH₄ and CO₂ gas with 99%, 98% and 95% purity from AFROX (Durban, SA) before analysing the biogas content.

Experimental design and setup

OCD was used for optimization in this study due to its ability to account for both mixture components and process variables. OCD is a hybrid of the Mixture and Response surface methods (RSM) in that it considers both the components of a mixture and the elements that may affect the entire process. By default, the functional connection between the dependent response and the independent variables/factors is quadratic-by-quadratic, indicating the mixture and process orders, respectively. The design was I-optimal with point exchange for the goal of predicting response surface methods and specific factor combinations. Fifteen (15) runs were generated using two mixtures and a single process component (temperature).

The design yielded four distinct mix ratios of 1:1, 3:1, 1:3, and 1:1 for SS to SW, respectively, and the three temperatures evaluated were room (25°C), mesophilic (35°C), and thermophilic (55°C), as shown in Table 1. The main objective was to determine the effect of altering the SS/SW mix ratio on biomethane yield and COD reduction.

Each bioreactor was filled with 400 mL of the inoculum and the requisite volume of the two substrates (SS and SW) according to the experimental design stated in Table 1. Each bioreactor contained 800 mL of mix-solution with a 180 mL headspace. Each bioreactor was purged with



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



nitrogen (N₂) gas for approximately 4 minutes to establish an anaerobic condition, and then put in the circulating water bath at the temperature indicated in Figure 1.

Table 1 Experimental design for Mixture ratio in the coded form with experimental and predicted yield and COD reduction for each run

Stand ard Run	SS(A)	SW(B)	TEMP(C) °C	Experimental Yield mL gCOD _t ⁻¹	Predicted Yield mL gCOD _t ⁻¹	Overall Volume of CH ₄ mg L ⁻¹	COD reduction
S ₆	0.75	0.25	55	43.81	44.25	343	84.55%
S ₁₄	0	1	35	88.76	95.78	695	57.85%
S ₇	0.5	0.5	55	80.96	80.63	634	32.69%
S ₅	0.5	0.5	35	131.74	127.08	1032	58.94%
S ₂	0	1	25	30.00	29.82	235	94.76%
S ₉	0.5	0.5	35	130.81	127.08	1024	59.13%
S ₁₅	0.75	0.25	35	144.50	157.86	1131	83.52%
S ₁	0.25	0.75	25	100.00	100.49	783	85.82%
S ₄	0.25	0.75	35	108.55	106.38	850	80.00%
S ₃	0.5	0.5	25	142.60	142.23	1117	94.38%
S ₁₂	1	0	55	26.34	26.18	206	20.15%
S ₁₀	0	1	55	208.30	208.35	1631	89.27%
S ₁₃	0	1	35	100.31	95.78	785	61.69%
S ₈	1	0	25	138.83	138.89	1087	95.15%
S ₁₁	1	0	35	204.00	198.72	1597	90.55%



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Using a downward water displacement technique, the connection tube on each bioreactor was connected to the water displacement/gas collection chamber. Each experimental run had a batch time of 30 days since the daily production for some reactors was <1% of the cumulative production as suggested by Holliger et al.²⁶

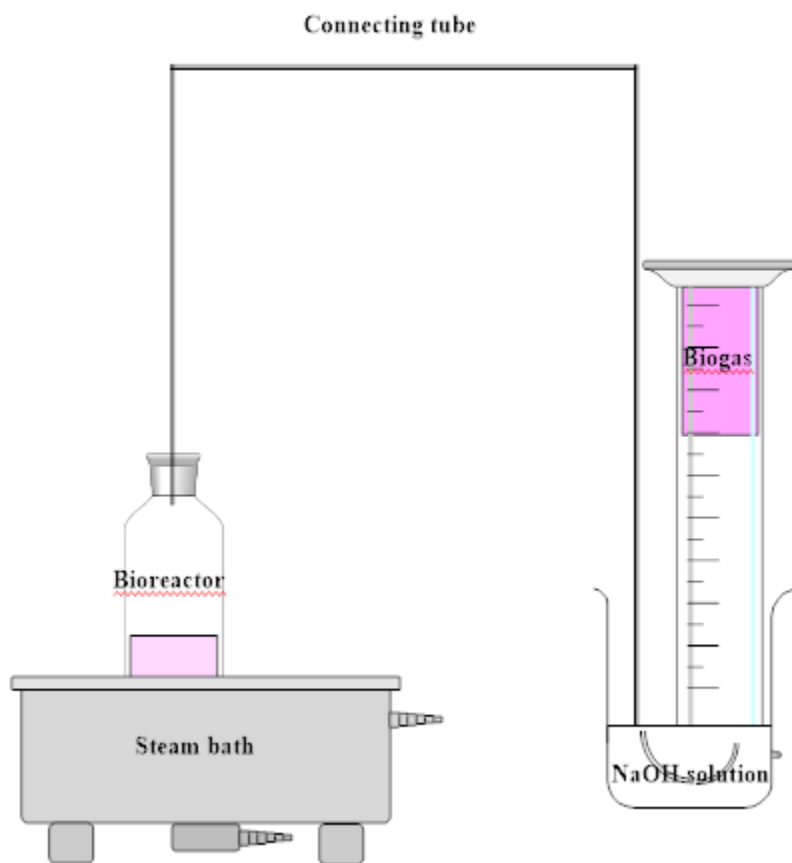


Figure 1 Schematic diagram of the Experimental run



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Results and Discussions

Characterization Result

This section describes the results of the substrate and inoculum characterization, with a pH of 5.97 ± 0.19 and 6.30 for SS and SW, respectively. The SW had a high COD of $7,130 \pm 260 \text{ mg L}^{-1}$ and a VS of $75.65 \% \text{ TS}$ with a TS of $4,515 \pm 97.5 \text{ mg L}^{-1}$, indicating its biodegradability potential, as did the SS, which had a TS, VS, and COD of $61,000 \pm 400 \text{ mg L}^{-1}$, $67.2 \% \text{ TS}$, and $3,400 \pm 200 \text{ mg L}^{-1}$, respectively.²⁷ The SS and SW results obtained were also within the range of those previously reported in the literature.^{28,29} The inoculum's pH, TS, and VS values of 7.19 ± 0.1 , $11,000 \text{ mg L}^{-1}$, and $54.6 \% \text{ TS}$, respectively, demonstrate its potential to supply microorganisms essential for the AD process.

COD removal efficiency

In this study, the COD reduction potential of the batch process was considered as it helped in determining the amount of COD removed. Table 1 shows the initial and final COD content of the assays. The highest COD reduction was observed for mono-digestion of each substrate, as demonstrated by runs S₈ and S₂, with 95.15 and 94.76%, respectively. Based on the mix-ratio, 94.38%, 85.82% and 84.55 COD reduction was obtained for S₃, S₁ and S₆ at 25°C and 55°C, respectively. Although no correlation was found between the mix-ratio and COD reduction percentage, it was discovered that temperature does play a role in COD reduction, as the most



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



COD reduction was observed at a temperature of 25°C when compared to other temperatures considered in this study.

However, the effect of pH on COD removal efficiency was also visible. When the pH of five (5) of the reactors was measured at the end of the digestion, it was found to be above the specified range for the AD process. It was discovered that four (4) of these runs, namely S₉, S₁₄, S₇, and S₁₂, had a percent COD reduction of 59.13, 57.85, 32.69, and 20.15%, respectively. Similarly, one of these runs had the lowest biomethane production, which may be attributed to the pH change.²⁸ Figure 2 depicts the pH at the start and end of the process. The initial pH of all experimental runs was within the optimum range for the AD process, but the final pH of some of the runs was outside the range, which could account for the instability and low productivity of these specific runs.

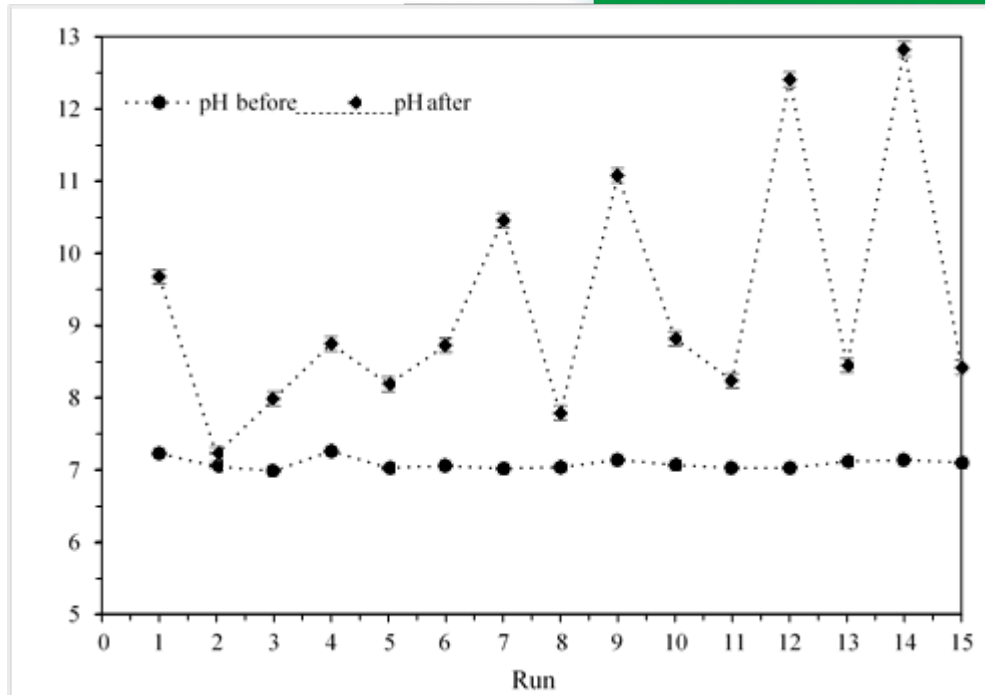


Figure 2 pH change before and after the digestion process for all runs

Statistical Analysis of the model

Table 1 shows the experimental and predicted yields of biomethane ($\text{mL CH}_4 \text{ g CODt}^{-1}$) as well as the percentage reduction in COD. The CH_4 yield was calculated by dividing the total CH_4 production by the initial amount of COD in each reactor. The statistical model best suited for the methane yield from the fit summary table was the quadratic-by-quadratic model (mixture by process order) as shown in Equation 1 and 2 for coded and actual values. According to the analysis of variance (ANOVA), the model obtained for methane yield was significant as p-value is less than 0.05, as shown in Table 2. The f-value of 0.3785 indicates that the lack of fit was not



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Table 2 ANOVA for Biomethane Yield by Quadratic * Quadratic Model

Source	Sum of Squares	^c df	Mean Square	^d F-value	^e p-value	comments
Model	41384.11	8	5173.01	97.87	< 0.0001	significant
⁽¹⁾ Linear Mixture	240.14	1	240.14	4.54	0.0771	
AB	1624.28	1	1624.28	30.73	0.0015	
AC	6654.85	1	6654.85	125.90	< 0.0001	
BC	16697.08	1	16697.08	315.88	< 0.0001	
ABC	3509.06	1	3509.06	66.39	0.0002	
AC ²	6682.20	1	6682.20	126.42	< 0.0001	
BC ²	42.14	1	42.14	0.7972	0.4063	
ABC ²	1467.72	1	1467.72	27.77	0.0019	
Residual	317.15	6	52.86			
Lack of Fit	250.02	4	62.50	1.86	0.3785	not significant
Pure Error	67.13	2	33.57			
Cor Total	41701.27	14				
Standard Deviation	7.27		R ²	0.9924	Adjusted R ²	0.9823
Adeq Precision	32.3492		Predicted R ²	0.9370		

⁽¹⁾ Inference for linear mixtures uses Type I sums of squares.

^c Degree of freedom (df).

^d Fisher's precise test value (F-value)

^e Probability value

significant, and a non-significant lack of fit is desirable for the model to be acceptable. The methane yield had a 99.24% variability, as shown by an R² value of 0.9924 with an adequate



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



precision of 32.35, indicating that the model can be used to predict the methane yield easily. The regression model terms were all significant apart from BC² whose p-value was greater than 0.05.

$$Yield = 192.11 A + 126.34 B - 166.96 AB - 56.36 AC + 89.27 BC - 189.02 ABC - 109.58 AC^2 - 7.25 BC^2 + 209.45 ABC^2 \dots\dots\dots Equation 1$$

$$Yield = - 436.80876 SS - 163.29319 SW + 1826.49907 SS * SW + 35.20310 SS * Temperature + 8.53027 SW * Temperature - 87.07154 SS * SW * Temperature - 0.487003 SS * Temperature^2 - 0.032237 SW * Temperature^2 + 0.930878 SS * SW * Temperature^2 \dots\dots\dots Equation 2$$

Influence of substrates and temperature interaction on the biomethane yield

Figure 3 depicts the 3D plot for the CH₄ yield as a function of substrate interaction with temperature. As shown in figure 3, there is a synergy between an increase in SW and an increase in temperature on yield, as an increase in temperature and SW produces an increase in yield, and higher temperatures appear to favour SW methane yield. The interaction term for temperature and SW had a positive effect on the yield, as indicated by the approximate coefficient of 8.53 in Equation 2. Figure 3 also shows that a higher temperature and an increase in the SS fraction in the mix could lead to process inhibition, halting the yield. As a result, lowering the temperature and increasing the SS may result in an increase in biomethane yield. This can also be seen if the temperature is raised while the SS decreases, as indicated by the coefficient estimate of 35.2 in Equation 2. For optimal CH₄ yield, there is an inverse relationship between the SS ratio and

temperature, this could be because the inoculum used in this study was obtained from a digester operating at 25°C, which the microorganisms are accustomed to.

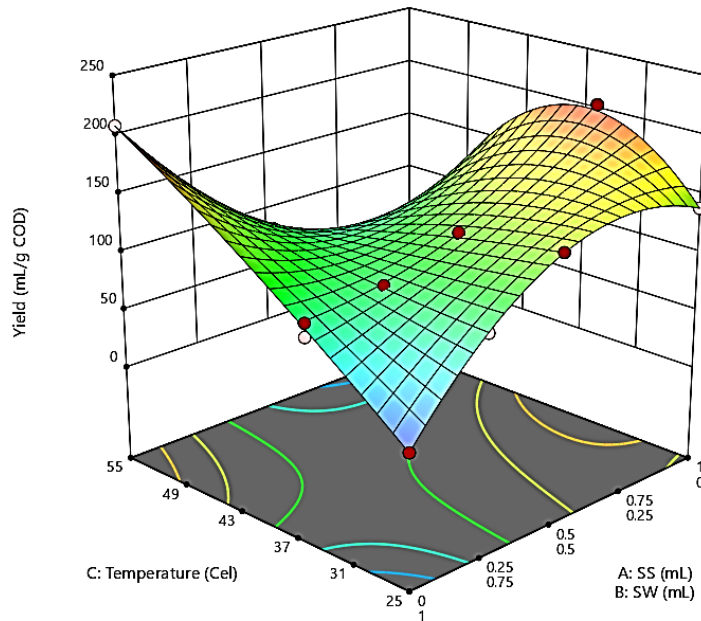


Figure 3 The 3D mix plot of CH₄ Yield for SW mix

Influence of co-substrates synergism on the biomethane yield

Based on the results, it was discovered that the addition of SW increases the yield of biomethane. As shown in Figure 4, an increase in the volume fraction of SW to SS corresponds to an antagonist behaviour in biomethane yield. When the volume fraction of SW was between 0 and 0.25, the yield increased, whereas an increase until 0.75 resulted in a decrease in the yield, the initial increase could be attributed to balanced moisture content while the succeeding decrease in yield



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13-15 December 2021



with increase in SW could be due to inhibition which is only broken down by an increase in temperature. In the latter case, increasing the fraction of SW resulted in a decrease in yield, possibly due to a lack of sufficient substrate (in terms of VS) for the microorganisms supplied by the SS to act on.

Table 2 shows that the p-value for the interaction of SW and SS on a quadratic scale is insignificant (0.4063) but significant on the linear scale. Equation 2 reveals a negative coefficient (-87.07) for the synergetic effect of SS and SW when temperature is involved, which had a negative effect on CH₄ yield when all other terms were held constant. Though overall, the synergetic effect of SW and SS have a profound effect on the yield as seen in equation 2 with a higher coefficient of 1826.5 and likewise in figure 4 with the highest yield of 155 mL g COD⁻¹.

Numerical Optimization

The optimum condition for the factor as well as the mix-ratio was determined using the equation derived from the OCD and a numerical optimization tool. The optimization criteria were to obtain the highest possible yield of CH₄ with a focus on supplementing the SS with little SW and the aim of running the reactor at lower temperature. The optimum biomethane yield was 156.96 mL g COD_t⁻¹ with a desirability of 84.7% as shown in Figure 5. As a result, the optimal conditions are a mix-ratio of 2.3:1 (SS: SW) and a temperature of 28.7°C.

Table 3 summarises previous research on the AcoD of SS with industrial effluent conducted by different authors. It can be shown that when SW was used as a co-substrate for SS, the CH₄ output



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was increased, suggesting the efficiency of SW as a co-substrate for SS. The discrepancies in results, however, could be attributable to the use of different wastewater, the number of experiments, and the units of calculation. The experimental conditions and the results obtained in each case are presented.

Table 3 Comparative studies on the process conditions and yield of CH₄ from AcoD of SS and industrial wastewaters

Substrates used	Inoculum	Reactor type, volume	Condition for maximum methane yield	Reference
SS and Animal by-products (ABP)		Batch, 5L	35°C, 3:1 (SS:ABP) for 473.99 mL g VS ⁻¹ 35°C,	13
SS and SW-DW	Anaerobic digested sludge	Batch, 250mL	1:1(SS:SW-DW) for 154 mL gCOD ⁻¹ 28.7°C,	15
SS and SW	Anaerobic digested sludge	Batch , 1 L	2.3:1(SS:SW) for 156.96 mL gCOD ⁻¹	This Study



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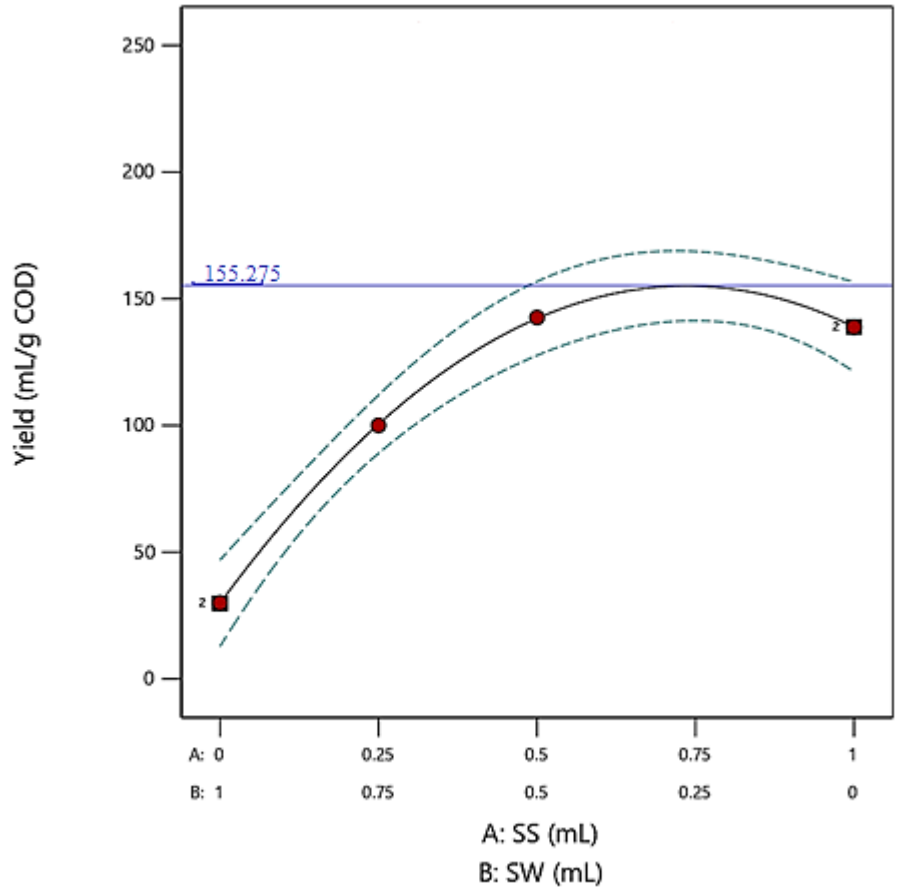


Figure 4 Effect of SW and SS mix

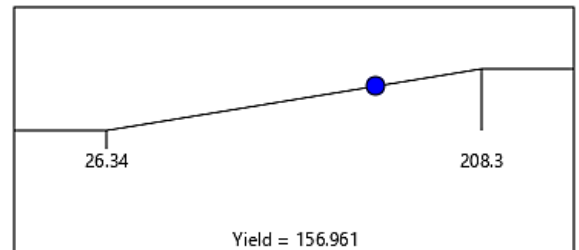
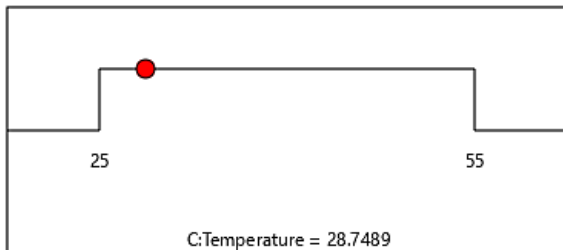
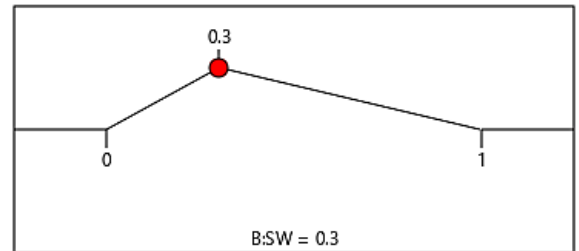
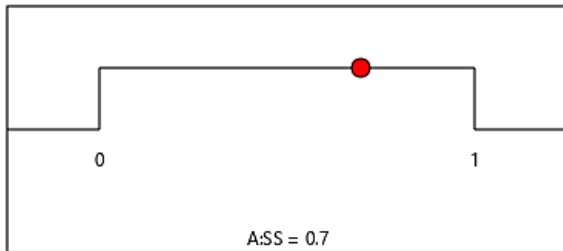


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Cape Town, South Africa
13-15 December 2021



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Desirability = 0.847

Figure 5 Ramp plot for Optimum Solution for Maximization of CH₄ Yield

Conclusion

In this study, the effect of SW addition as a co-substrate to SS on biomethane production enhancement was investigated, and the optimal mix-ratio for both substrates was determined using OCD and numerical optimization. At 28.7°C and a mix-ratio of 2.3:1, the highest biomethane yield of 156.96 mLCH₄ g COD_r⁻¹ was obtained (SS: SW). The results showed that adding SW improves



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13-15 December 2021



the yield of biomethane from the AcoD of SS. Similarly, the effect of pH has been demonstrated to be a determinant of process stability, thereby influencing CH₄ yield. Likewise, the dual effect of both enhancing the yield as well as reducing the COD content of the wastewater was achieved, thereby, reducing pollution as well as generating renewable energy. The OCD tool was found to be useful because the results indicate that the model was adequate and accurate in predicting biomethane yield within the design space.

Acknowledgements

The National Research Foundation (NRF) block grants UID118686 scholarship fund and the Durban University of Technology (DUT) funded this study.

Conflict of interest

The authors declare no conflict of interest.

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13-15 December 2021



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Cape Town, South Africa
13-15 December 2021



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13-15 December 2021



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A Simulation Study of the Combined Process of Torrefaction and Gasification of Lignocellulose Biomass (Bagasse) for Syngas and Methanol Production

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Abstract

Biomass is an underutilized energy resource that now supplies around 10% of the world's energy and has the potential to meet more than 25% of the world's energy demand by 2035. Methanol is one of the most important organic compounds in the chemical industry, as it is used as a raw material to make several industrial chemicals. This study investigates a comprehensive process for the co-production of syngas and/or methanol from bagasse. Overall, four scenarios were considered in this study, they are bagasse gasification for syngas production with torrefaction (S1), bagasse gasification for the co-production of methanol and syngas with torrefaction (S2) while the other two (S3 & S4) are without torrefaction process. The gasification process was modelled in Aspen Plus using a kinetic-free equilibrium model using steam and pure oxygen as the gasification agent. For the syngas cleaning, the rectisol process was employed while for the methanol synthesis, hydrogenation reactions of CO₂ and CO coupled with the water gas shift reaction were employed. From the result obtained, the process involving torrefaction has more syngas yield hence more methanol was synthesized (0.37kg_{MeOH}/kg_{Bagasse}) when compared to the process without torrefaction (0.33kg_{MeOH}/kg_{Bagasse}). The syngas from the torrefaction processes also have higher



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lower heating values (LHV) of 9.24 MJ/kg and 8.76 MJ/kg for S1 and S2, when compared to that without torrefaction (S3 & S4) with LHV of 9.07MJ/kg and 8.58 MJ/kg respectively. In addition, the S1, S2, S3, and S4 have the tendency of generation energy of 17.67 MW, 20.33 MW, 17.46 MW, and 19.30 MW respectively. Hence, the process with torrefaction has proven to be an ideal pretreatment process for syngas and/or methanol production from bagasse gasification.

1.0 Introduction

The most abundant renewable feedstock, lignocellulosic biomass (LCB), is far less expensive than crude oil. [2]. LCB generally inexpensive can be replenished in a sustainable manner [3]. The development of renewable energy derived from LCB as a fossil fuel substitute is ultimately necessary for human survival [4]. As a result, there has been a surge in interest in creating LCB-derived products including alcohols and syngas. The development of renewable energy derived from LCB as a fossil fuel alternative is ultimately necessary for the human race's survival [4]. In 2012, the United States had around 340 million metric tonnes of LCB accessible for bioenergy production, with 70% coming from agricultural wastes [5]. Due to the quest for renewable and "carbon-neutral" energy, LCB has recently garnered significant interest as a feedstock for anaerobic digestion [6].

In torrefaction, raw biomass is cooked slowly in an inert atmosphere at a temperature range of 200 - 300 °C similar to a low heating rate pyrolysis method [7, 8]. LCB such as sugarcane consists primarily of lignocellulosic polymers such as hemicellulose, cellulose, and lignin, each of which decomposes at various temperatures. Torrefaction has been shown to have a major effect on this hemicellulose, whereas cellulose and lignin are affected to varying degrees depending on torrefaction temperature and hold time [9, 10]. The purpose of the torrefaction was to see how different constant torrefaction temperatures affected moisture and volatile content, calorific value, fixed carbon composition, and grindability [11, 12].



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Gasification on the other hand is a process that produces carbon monoxide, hydrogen, methane, and carbon dioxide from organic or fossil-based carbonaceous materials [13]. This is accomplished by reacting the material at high temperatures, often exceeding 1000 °C, with a small amount of oxygen and/or steam. Gasification relies on partial oxidation at very high temperatures in the conversion of solid biomass into energy [14]. Bagasse syngas is suitable for use in stationary gas turbines. Because syngas can be combusted at higher temperatures or even in fuel cells, gasification has the potential to be more efficient than direct burning of the original fuel [13]. Sugarcane bagasse gasification contributes to the development of sustainable renewable energy sources. Thus, this study proposes to assess the feasibility of the combined process of torrefaction and gasification of bagasse for syngas and methanol production.

2.0 Methodology

A. 2.1 Bagasse characteristics

The proximate, ultimate analysis and the heating value of the raw and torrefied sugarcane bagasse employed in this study was obtained in a previous study by Anukam *et al.* (2018) [14] as presented in Table 1.

Table 1. Bagasse Proximate and Ultimate Analysis (wt.%) [14]

Components	Raw	Torrefied (300 °C)
Moisture Content (MC)	1.08	0.87
Volatile Matter (VM)	73.73	54.07
Fixed Carbon (FC)	23.87	28.45
Ash	1.32	16.61
N	0.20	1.80
C	44.10	56.16



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Cape Town, South Africa
13-15 December 2021



H	5.70	3.94
S	2.30	0.01
O*	47.70	37.27
Heating Value (MJ/kg)	17.86	20.19

*Obtained by difference

B. 2.2 Process description

This study is focused on the design of a comprehensive simulation process model for the production of methanol, syngas, as well as the co-production of both using Aspen plus software. Four scenarios were considered in the process, they are bagasse gasification with torrefaction and without torrefaction process. In the first scenario (S1), it involves syngas production only through torrefaction and gasification as shown by the Aspen plus flowsheet in Fig. 1b. Here, four distinct units were identified; they include the pretreatment (torrefaction) unit, the gasification, the gas cleaning/post-treatment (rectisol) unit and the methanol synthesis unit). The second scenario (S2) involves syngas and methanol production through the combined process of torrefaction and gasification as shown by the Aspen plus flowsheet in Fig. 1a. Here, only two distinct units were identified; the torrefaction and the gasification units. The third scenario (S3) involves syngas production through the process of gasification only. In the last scenario (S4), the co-production of syngas and methanol is involved. Only two distinct units were identified in S3 and S4; the decomposition and the gasification units.

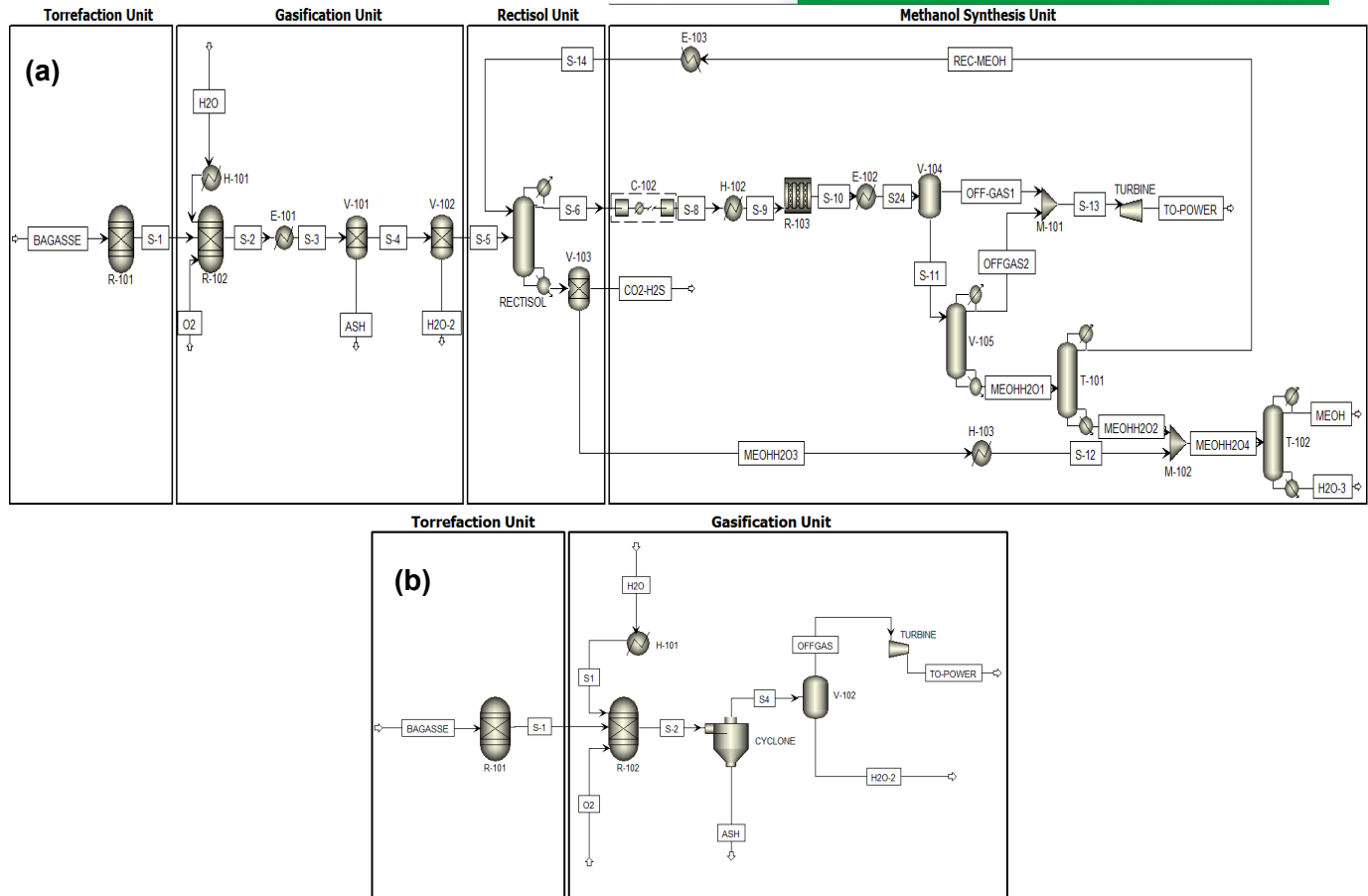


Fig. 1. Aspen plus process flowsheet (a) methanol and syngas (b) syngas only.

The basic assumptions in the gasification process simulation employed in this study include:

1. The gasification process is assumed to be steady-state, isothermal and occur at constant atmospheric pressure [15].
2. The decomposition zone is assumed to be zero-dimensional, implying that particle motion is distributed spatially in all directions. As a result, the reactor geometry cannot be reflected [16].
3. Devolatilization occurs simultaneously and the volatile products which mainly include CO, CO₂, H₂, CH₄, H₂S, NH₃, and H₂O [17].



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13-15 December 2021



4. All the gases are ideal and are uniformly distributed in gaseous phase [17].
5. The gas reactions take place at a chemical equilibrium state and pressure drops are neglected [17, 18].
6. Tar formation was neglected [19].

C. 2.3 General simulation description

Bagasse is firstly torrefied [20], before being fed to the gasification reactor for the scenarios (S1 and S2) that requires torrefaction while feed decomposition reactor was employed for the scenarios without torrefaction process (S3 and S4). The steam and oxygen (from the ASU) were fed to the gasifier with steam to biomass ratio (SBR) and equivalence ratio (ER) of 0.76 and 0.20 respectively as obtained from Pedersen *et al.* 2015 [21]. The gasification process was modelled in Aspen Plus using a kinetic-free equilibrium model. The non-conventional feed was fed into the R-101 reactor (in pretreatment case) before entering the R-102 (the gasification reactor). The pre-heated steam and oxygen which serves the gasification agents enters the R-102. As earlier mentioned, the gasification RGibbs reactor was handled the computation of the syngas generation by the specification of the gasification reactions. The syngas generated from the R-101 is then cooled in the E-101 (which serves as an HRSG) afterwards before ash and steam is separated from the stream using the V-101 and V-102 [20, 22]. The total heat required for steam generation from the syngas cooling was determined by simulating a heat exchanger with dew-point specification [23, 24]. The rectisol unit was modelled using the Aspen Plus component separator (RECTISOL). Here, the syngas leaving the separator (V-102) is absorbed by chilled methanol stream in the column. The exit gas stream from compressed syngas and heated before going to the methanol reactor (R-103) while the acid gas rich stream exit through the column bottom stream. In other to have a full methanol recovery, a separator (V-103) was used to separate the acid gas (CO₂-H₂S) from the methanol. Using the Redlich–Kwong–Soave–BM equation of state for methanol, the separation of residual gases from methanol synthesis products (in liquid state) was simulated as flash drums [22]. As previously reported [21, 24, 25], simulations of power generation using a gas turbine



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13-15 December 2021



using unconverted/unrecycled syngas and the subsequent combined (steam) cycle were carried out. The energy demands of supporting and gas-cleaning units in syngas production, such as the ASU, were obtained from Kreutz et al. (2008) [24] at 380 kWh/tonne per tonne of oxygen required, while the demands for a single stage Rectisol were obtained from Sun and Smith (2013) [23] at 7.57 kW thermal and 1.42 kW electrical energy per kilomole of acid gas in the syngas, respectively.

3.0 Result and Discussion

D. 3.1 Syngas composition, methanol yield, syngas LHV, CGE and Energy yield from the bagasse gasification processes

The simulation results from the four scenarios (S1 - S4) were compared in terms of the syngas composition, methanol yield, syngas LHV, the cold gas efficiency (CGE) as well as the energy yield. The gasification processes that involved syngas production only (S1 and S3) have the highest syngas composition with a combined total (H_2+CO) of 80.6% and 79.6% respectively. This also shows that the torrefaction process improves the CO component of the syngas; meanwhile the process without torrefaction has a slightly higher H_2 component as shown in Fig 2. The gasification processes for the co-production process only (S2 and S4) have combined syngas composition of 75.5% and 75.0% respectively. The methanol yields from S1 and S3 are 33.9 mol% and 31.2 mol % respectively and this is equivalent to $0.37 \text{ kg}_{MeOH}/\text{kg}_{Bagasse}$ and $0.33 \text{ kg}_{MeOH}/\text{kg}_{Bagasse}$ respectively. In addition, S1 and S3 produced the highest syngas LHVs with $9.24 \text{ Nm}^3/\text{kg}$ and $9.07 \text{ Nm}^3/\text{kg}$ respectively while S2 and S4 produced LHVs of 8.76 and 8.58 respectively as shown in Fig. 2.

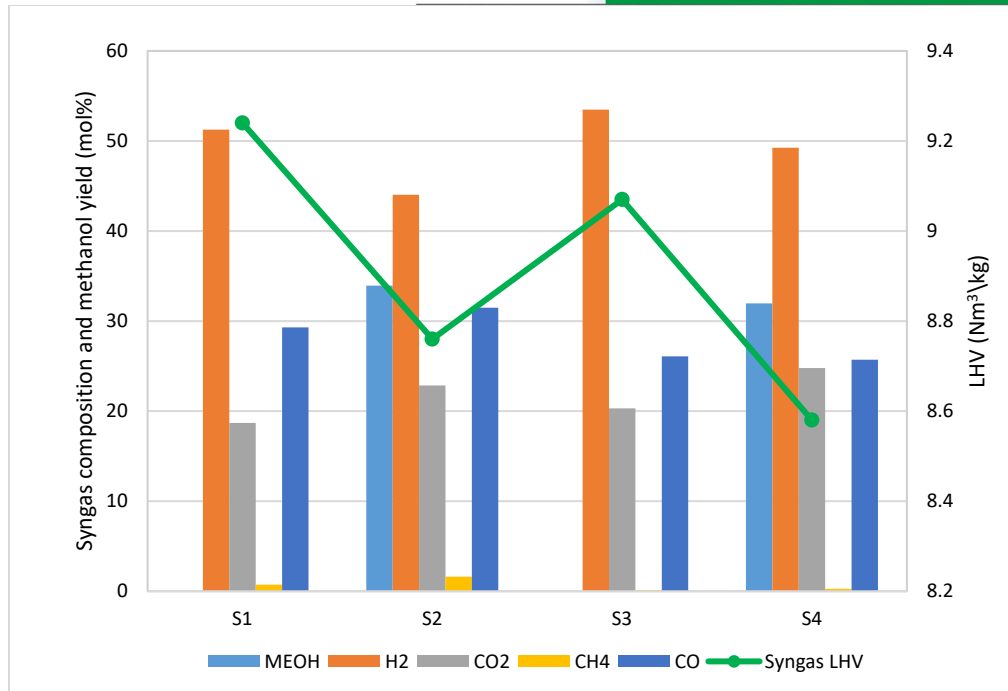


Fig. 2. Product yield from the four scenarios.

The cold gas efficiency (CGE) of the processes were also compared against each other as shown in Fig. 3. S1 has the highest CGE with 72.1% while S4 has the lowest with 32%. It should be noted that CGE is a function of the syngas yield and heating value, hence, the combined process of methanol and electricity process will have a very low CGE since most of the syngas produced after the gasification process have been converted to methanol. In addition, the S1, S2, S3, and S4 have the tendency of generation energy of 17.67 MW, 20.33 MW, 17.46 MW, and 19.30 MW respectively. Overall, the process with torrefaction has proven to be an ideal pretreatment process for the generation of syngas and/or methanol production from bagasse gasification.



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Cape Town, South Africa
13-15 December 2021

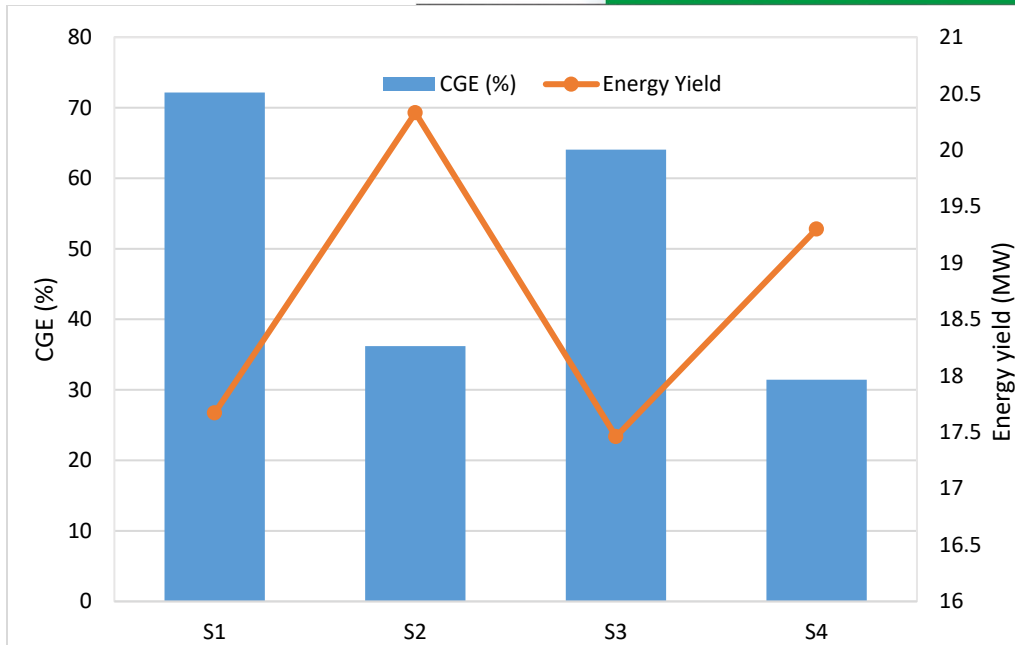


Fig. 3. Cold gas efficiencies from the four scenarios (S1 - S4).

E. 3.3 Result validation with related studies

The final product stream from the combined processes of methanol and syngas production was also validated with the works of Petersen et al. (2015) and Puig-Gamero et al. (2018) as shown in Fig. 4. It can be seen that torrefied process (S2) produced more methanol (33.9 mol %) than the processes without torrefaction including the previous authors. S4 has methanol composition of 31.9 mol %, Petersen et al. (2015) reported and Puig-Gamero et al. (2018) both reported methanol composition of 33 mol % and 28 mol % respectively. In terms of H₂ co-production with methanol, the direct gasification processes (S4, Petersen et al., and Puig-Gamero et al. yielded more H₂ with 33.5 mol %, 31.5 mol % and 29.5 mol % respectively while the torrefied process (S2) produced the least H₂ with 29.1 mol %. Finally, for syngas (CO+H₂) and methanol co-production, the direct process (S4) has more syngas composition. The variation with Puig-Gamero et al. is as a result of the different feedstock sample as well as the gasification syngas pretreatment process employed by the authors.

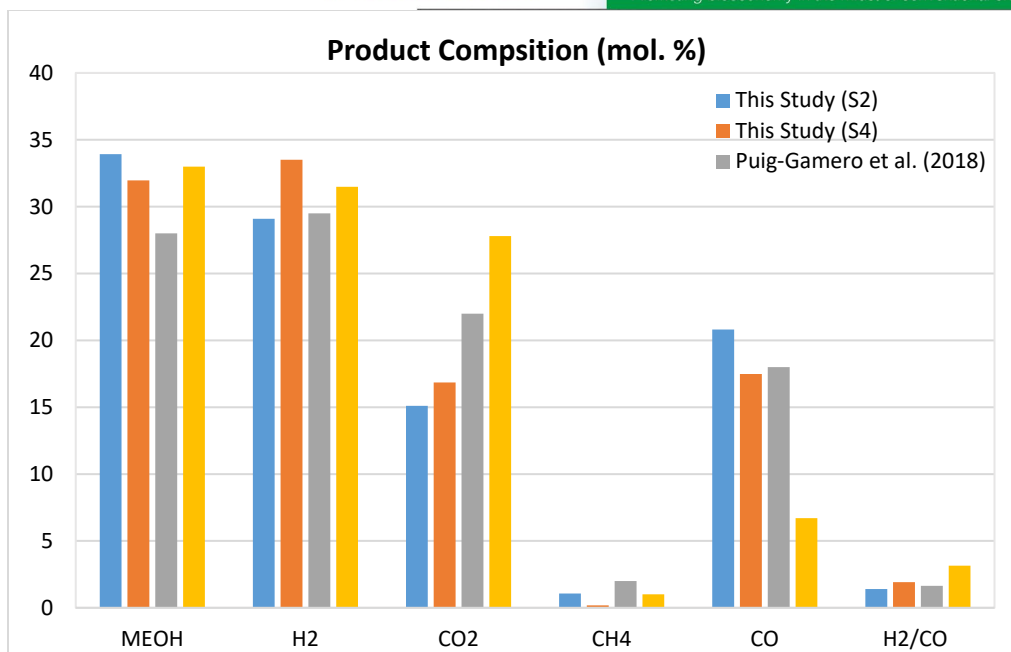


Fig. 4. Final product composition comparison with previous studies.

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1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



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1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Promoting bioeconomy in the midst of conventional energy resources

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1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



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Acknowledgements

The authors would like to thank the University of Johannesburg for their support.



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Cape Town, South Africa
13-15 December 2021



Experimental investigations on utilisation of ethanol-methanol (M25E75) blend as fuel in an automotive spark ignition engine.

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Abstract

An experimental investigation was carried out on a single-cylinder automotive spark ignition engine to study its combustion, performance, and emission characteristics using ethanol (E100) and ethanol-methanol blend (M25E75) as fuel. The engine speed was varied from 3500 rpm to 4200 rpm. The spark timing with E100 and M25E75 was advanced than gasoline. The experimental results indicate that In-cylinder peak pressure with E100 increased by 10% while with the M25E75 blend, and it was almost equal to gasoline. Ignition delay was almost similar with all the fuels. The combustion duration was slightly shorter by 5% with the blend as compared to gasoline. Combustion duration was the shortest with E100. MFB profile of E100 indicated that 10% and 50% mass burnt was earlier than gasoline due to its higher flame speed. MFB profile of M25E75 blend revealed that 10% mass burnt in shorter time duration while 50% and 90% burn durations were similar to gasoline. Brake specific fuel consumption (BSFC) with E100 increased by more than 20% than gasoline at all the speeds. BSFC with the blend and E100 were marginally equal. BSFC enhanced due to lower calorific value of E100 and M25E75 blend. Brake specific energy consumption (BSEC) decreased by 10-23% and 18-30% with E100 and M25E75 as compared to gasoline at different speeds. Brake thermal efficiency (BTE) of the engine increased



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Cape Town, South Africa
13-15 December 2021



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by more than 25% with the blend as compared to gasoline. BTE of the engine improved by more than 22% with E100 as compared to base gasoline. The volumetric efficiency increased by 6% and 24.7% at 3800 and 4200 rpm with M25E75 as compared to gasoline. A marginal increase of 3%-11% was observed with E100. Hydrocarbon (HC) emission increased by 1.5 times with E100 than gasoline due to enhanced flame quenching as a result of the cooling effect produced by E100. HC emission with M25E75 blend was slightly equal with gasoline. Nitrogen oxide (NO_x) emissions decreased by 60-70% with E100 than gasoline. The emissions decreased significantly by more than 75% with the M25E75 blend as compared to gasoline. Carbon monoxide (CO) emission with E100 decreased by 48% and 84% at 3800 and 4200 rpm respectively as compared to gasoline. CO emission measured with M25E75 was significantly lower by more than 80% than gasoline. It was concluded from the study that with M25E75 blend combustion, performance as well as emission characteristics of the engine are improved. The blend can work as a better substitute for the E100 fuel as well as gasoline at the places where the availability of pure ethanol is not abundant to fulfill the fuel demand.

Keywords: Ethanol (E100), Spark Ignition Engine, Spark Timing, Blend, Emissions, Methanol, Performance, Combustion.

Introduction

Energy security is one of the major global concerns. The conventional fuels such as diesel and petrol are limited and their utilisation is subjected to various stringent norms to prevent atmospheric pollution. In this context, various alternative fuels are being sought and tested which can replace the conventional ones and remain safe from the environmental point of view as well. Alcohol is being used as fuel in internal combustion engines for more than 100 years [1]. They can be efficiently produced from biomass and therefore, they are renewable and can be regarded



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



as carbon neutral. Alcohols such as methanol, ethanol, butanol and their several blends with gasoline can be used as fuel in a spark ignition (SI) engine. Alcohol fuels and particularly ethanol is produced from the fermentation of starch and cellulose present in the biomass including corn, barley and sugarcane which is known as the first generation of ethanol. Even waste biomass such as molasses, rice husk and bagasse can also be used to produce ethanol. That is known as second-generation ethanol. Ethanol is largely mixed with the gasoline to improve its octane rating. It is suitable to be used in a high compression ratio (CR) SI engine since the octane number (108) is very high. As compared to gasoline, the carbon content of ethanol is lower and oxygen content (34% by mass) is higher. The presence of oxygen enhances the combustion efficiency of ethanol. The high latent heat of ethanol helps lower down the heat losses that occur through the cylinder wall. The flame velocity of ethanol (0.61 m/s) is higher than gasoline (0.4 m/s) which helps achieve fast combustion. Ethanol is being used globally in neat form as well as blended with gasoline [1]. It is mixed with gasoline in different ratios to form blend fuels such as E5, E10, E15, E30, E85. Mohammed et al. [2] studied the effect of using different ethanol-gasoline blends (E10, E20, E30, E40) on the performance and emission characteristics of a spark ignition engine. The speed of the engine was varied from 1500 to 2500 rpm and the compression ratio was fixed at 8.5:1. They reported that brake thermal efficiency (BTE) of the engine increased as the ethanol percentage increased in the blend due to the higher flame velocity of ethanol. The emissions of carbon monoxide (CO), hydrocarbon (HC) and oxides of nitrogen (NO_x) were decreased with the blends as compared to gasoline. The maximum decrease of CO was 26.3% in E30. Maximum decrease of HC, CO₂, NO_x and CO₂ emissions was noticed with the E40 blend. Volumetric efficiency dropped with the blends as compared to gasoline. Ilham et al. [3] experimentally studied the effect of ethanol on the performance and emissions of a spark ignition engine. The experiments were conducted at a constant speed of 1500 rpm at partial loads of 25% and 50% at different excess air ratios (.8 to 1.3). BTE of the engine was higher with ethanol than gasoline at



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



all the excess air ratios. Unburnt HC emission decreased from 4 to 2.3 g/kWh and NO emission decreased from 9 to 4 g/kWh with ethanol than base gasoline. At 0.8 excess air ratio, the peak cylinder pressure with ethanol was slightly lower than gasoline due to high latent of ethanol which decreased the average cylinder temperature. A similar kind of study is reported by Phuangwongtrakul et al. [4] who investigated the SI engine performance fuelled with various ethanol-gasoline blends. They concluded that maximum torque at a lower speed could be achieved with an ethanol-gasoline blend if an optimal quantity of ethanol is used. Sakhivel et al. [5] reported that the E30 blend was better as fuel than gasoline for a SI engine. Literature reported on utilisation of pure ethanol as fuel in a SI engine are very scanty. Furthermore, a fact that engine modifications are required to take full advantage of pure ethanol, cannot be denied. Redesigning of the intake manifold of engine for enhancing evaporation of ethanol, improvement in cold-start ability, and increase of compression ratio engine are some of the modifications [1]. Costa and Sodre [6] reported that engine torque, brake mean effective pressure (BMEP), and output power was substantially improved with increased compression ratio at high speeds for both, E22 and hydrous ethanol. Balki et al. [7] investigated the performance, combustion, and emission characteristics in SI engine with a CR of 8.5:1. Fuel air ratio was controlled through carburettor keeping an equivalence ratio of 1. They reported that the combustion efficiency of the engine was better with ethanol and methanol fuels as compared to gasoline. With methanol and ethanol, NO_x and CO and HC emissions reduced by 49% and 47.6%; 22.6% and 21.25%; 21.6% and 19.13%; while CO₂ emissions increased by 4.4% and 2.51%, respectively, compared to gasoline. Combustion duration was shorter with alcohol fuels. Peak cylinder pressure was higher with ethanol than gasoline at high engine speed (3600 rpm) while it was lower at low speed (1600 rpm). Celik [8] experimentally studied various blends of ethanol and gasoline (E25, E50, E75, E100) to select a suitable one for a high compression ratio SI engine with a carburettor fuel system and excess fuel-air ratio of 1. The CR was varied from 6:1 to 10:1. He reported that 4%



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



power is decreased with E100 as compared to base gasoline. CO₂ emissions with the blends and E100 were less than gasoline on account of lower carbon content in the fuels. A similar trend was observed with CO emission. HC emission was higher with E75 and E100 than base gasoline due to the high heat of vaporisation associated with ethanol. NO_x emission was lower with all the fuels than gasoline. He concluded that E50 was the most suitable blend for the engine. With E50 fuel, the engine power increased by 29% and the emissions of CO, CO₂, HC and NO_x decreased by 53, 10, 12 and 19%. Pourkhesalian et al. [9] studied the performance and emission characteristics of a SI engine fuelled with different alternative fuels including hydrogen, methane, methanol, ethanol and propane through simulation and validated the results through experiments. They reported that brake specific fuel consumption (BSFC) with ethanol was higher than gasoline. The power produced by ethanol was 10% lower than gasoline since volumetric efficiency was lower with ethanol. CO and NO_x emissions were higher with gasoline than ethanol. Balki and Sayin [10] studied the effect of the increase in compression ratio with pure ethanol and methanol. The CR was varied from 8.5:1 to 8:1, 9:1 and 9.5:1. They concluded that cylinder gas pressure is increased with the alcohols at each CR. The exhaust emissions were also lower with the alcohols as compared to base gasoline at all CRs. Numerous studies are available on the application of methanol gasoline blends in a spark ignition engine. Geng et al. [11] reported that with the M15 blend, combustion duration was shorter than gasoline. The combustion characteristics were improved with the blends. Similarly, it is reported that CO and HC emissions were decreased with M15 [12]. In addition to this, Zaid et al. [13] reported that with M3, M6, M12 and M15 blends, the brake thermal efficiency of the engine was improved and was better than gasoline. Various studies confirm that the performance of the engine is improved with the use of methanol-gasoline blends [14-20]. In addition to this, several studies are available on the use of gasoline-ethanol-methanol (GEM) blends in a SI engine. GEM blends are formulated in such a way that their properties match the E85 blend [21-22]. It can be inferred from the



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



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literature study that blends of ethanol-gasoline and methanol-gasoline and GEM improve the performance and decrease the emissions from the engines. Table 1 shows the basic difference in properties of ethanol, methanol and gasoline. It is clear from the literature review, that extensive work has been done on a SI engine fuelled with ethanol-gasoline and methanol-gasoline blends. However, experimental investigation on utilisation of ethanol-methanol blend in a SI engine is still not studied. The present work is dedicated to study utilisation of ethanol-methanol blend (M25E75) and its comparison with pure ethanol (E100) and gasoline.

Table 1. Properties of E100, M100 and gasoline

Table 1. Properties of E100, M100 and gasoline

Property	Gasoline	Methanol	Ethanol
Composition	C ₅ -C ₁₂	CH ₃ OH	C ₂ H ₅ OH
Density at 15°C, kg/m ³	750-765	792	790
RON Research octane number (min)	91-100	108.7	108
MON Motor octane number (min)	82-92	88.6	92
Auto Ignition Temperature °C	257	465	363
Boiling point °C	27-225	64.8	78.5
Latent heat of vaporisation, kJ/kg	305	1109	904
Low calorific value, MJ/kg	44	19.66	28
Stoichiometric air/fuel ratio	14.5	6.45	9
Laminar flame speed (cm/s)	33	52	39

Methodology and Experimental Details

An automotive single-cylinder spark ignition engine having cylinder capacity of 250 cm³ is used in this experimental study. The bore and stroke of the engine are 74 mm and 58 mm. The rated power and torque of the engine are 15 kW at 8000 rpm and 18 Nm at 6000 rpm respectively. The experimental setup has been shown in Figure 1 which consists of a port fuel injection system and ECU for controlling the engine parameters.

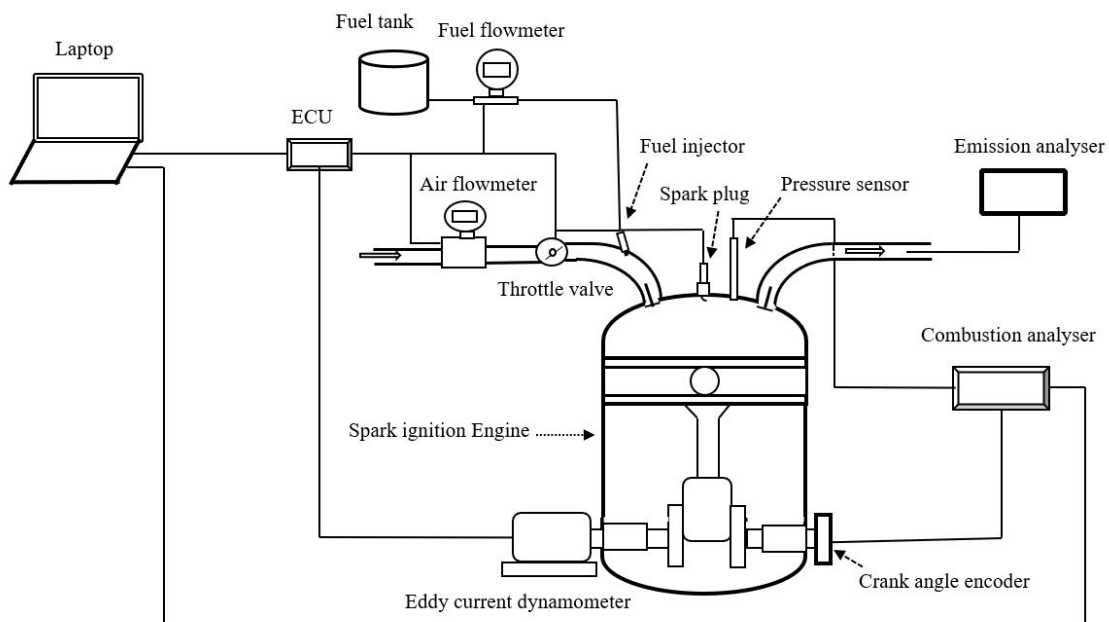


Figure 1- Schematic layout of the setup for experimental investigation



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Cape Town, South Africa
13-15 December 2021



An eddy current water-cooled dynamometer was used for loading the engine. AVL make exhaust gas emission analyser was used for measuring exhaust gas emissions. The engine was run at various speeds ranging from 3500-4200 rpm and a constant torque of 5 Nm. The results of the E100 and M25E75 blend (methanol 25% and ethanol 75% by volume) were compared with baseline gasoline. It is to be noticed that the engine was not modified for E100 and M25E75 fuels. The equivalence ratio was stoichiometric (1 ± 0.1) at all the operating points. The spark timing was advanced with E100 and M25E75 blend through engine control unit (ECU) than gasoline to operate at MBT. An optical crank angle encoder was attached with the dynamometer to measure crank angle signals. A piezoelectric transducer was attached to the engine head to capture In-cylinder pressure signals. AVL Indicom V2.9 was used for acquiring In-cylinder pressure data. Equations 1-5 were used for calculating combustion and performance parameters for the engine.

Heat release (Q) per degree crank angle (C.A) was calculated using Equation 1.

$$\frac{dQ}{d\theta} = \frac{\gamma}{\gamma-1} P \frac{dV}{d\theta} + \frac{1}{\gamma-1} V \frac{dP}{d\theta} + \frac{dQ_{ht}}{d\theta} \quad (1)$$

The cumulative heat release ($Q_{cum.}$) was calculated by using Equation 2.

$$Q_{cum.}(\theta) = Q_{\theta} + Q_{\theta-1} \quad (2)$$

The flame development angle (ignition delay) was calculated by Equation 3.

$$ID = \int_{Spark}^{SOC} d\theta \quad (3)$$

The flame propagation angle (combustion duration) was calculated by Equation 4.

$$CD = \int_{SOC}^{EOC} d\theta \quad (4)$$

The brake thermal efficiency of the engine is calculated using Equation 5.



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Cape Town, South Africa
13-15 December 2021



$$\eta_t = \frac{BP}{m_f \times C.V}$$

(5)

where

BP - brake power (W)

m_f - mass flow rate of fuel (kg/s)

C.V.- calorific value of fuel (J/kg)

Similarly, brake specific fuel consumption (BSFC) (g/kWh) and brake specific energy consumption (BSEC) (kJ/kWh) were calculated using mass flow rate of fuel and brake power.

Results and Discussion

Combustion characteristics

Fig. 2 shows the In-cylinder pressure variation with the crank angle at 3500 rpm for the M25E75, E100 and gasoline. Peak pressure is highest for E100 (27.6 bar) which is 10% higher than gasoline. The difference between peak pressures of the blend and gasoline is negligible. The higher flame velocity of ethanol is helpful in attaining near constant volume combustion. When piston moves towards TDC and spark is ignited, high flame velocity of fuel ensures faster combustion and pressure is enhanced.

The flame speed of methanol is higher than ethanol and gasoline. The rate of chemical reactions plays a major role in determining flame speed and thus combustion of any fuel. Alcohol addition increases the volatility of the fuel which improves the atomisation and mixing of air-fuel that improves the combustion and thus peak pressure is enhanced. When methanol (10-30% concentration) is mixed with ethanol, then hydrogen bonding between the two molecules is

increased while intermolecular forces decrease due to the formation of multimer structures through dispersion forces in the ethanol molecule [23]. However, studies on flame speed and combustion of ethanol-methanol mixtures are not available in the literature to ascertain the molecular phenomenon between the two alcohols.

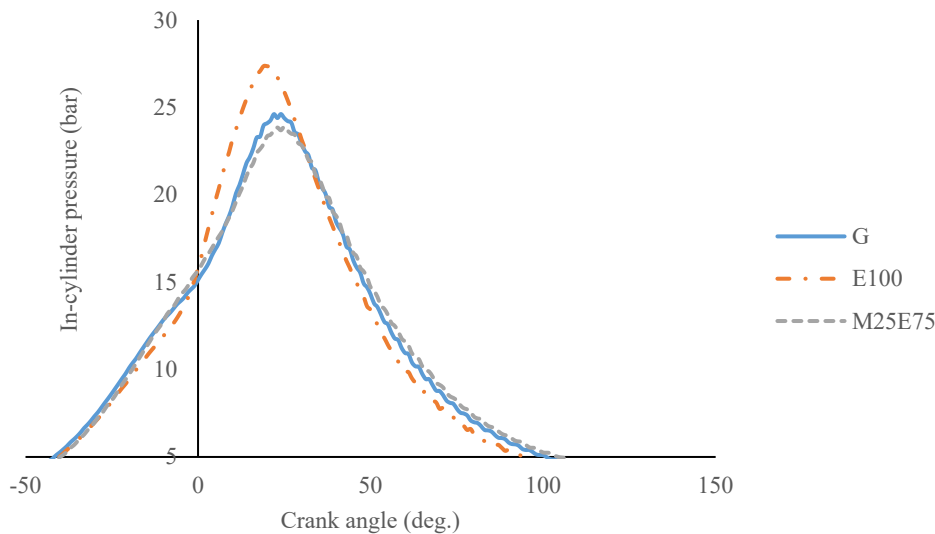


Fig. 2 Pressure and crank angle curve at 3500 rpm

Fig. 3 indicates the mass fraction burnt (MFB) profiles with E100, M25E75, and gasoline. 10% and 50% mass fraction burnt are highlighted. With E100 and M25E75, 10% mass fraction burnt is much before 10 degrees crank angle while with gasoline, this duration is more. With E100, the same trend is followed till 50% and 90% burn. It can be attributed to the fact that the minimum ignition energy of methanol is much less (0.14 mJ) than ethanol (0.23mJ) and gasoline (0.25mJ). Therefore, due to the presence of methanol in the blend, the ignition is quick and the rate of chemical reactions is enhanced. However, later on till 90% MFB, flame speed plays an important role.



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Cape Town, South Africa
13-15 December 2021



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The MFB profile of the blend resembled the gasoline after 10% burnt fraction. Fig. 4 indicates the cumulative heat release curve for all the fuels. Cumulative heat release with M25E75 blend is the highest by 12% than gasoline. The difference in cumulative heat release with E100 and gasoline is negligible. It is the total amount of heat generated in a cycle during the combustion of fuel.

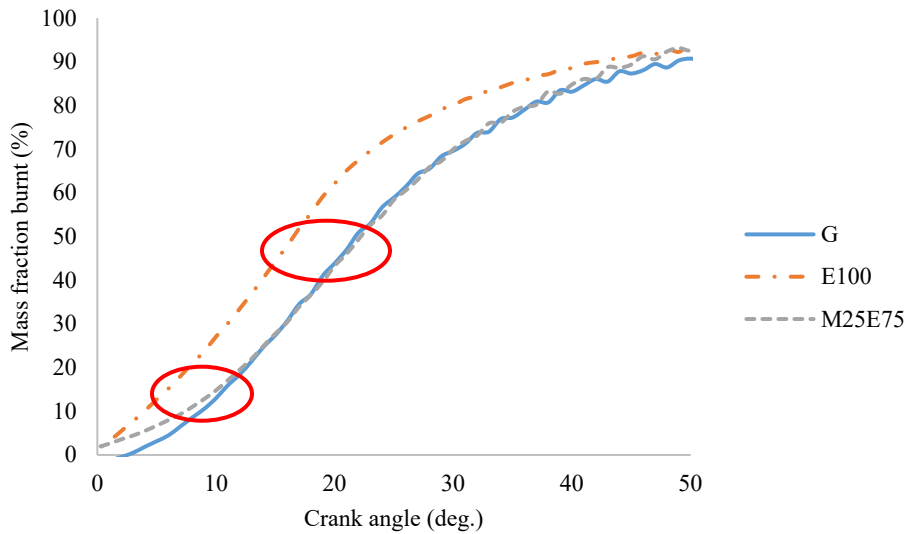


Fig. 3 Mass fraction burnt profiles with different fuels



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Cape Town, South Africa
13-15 December 2021



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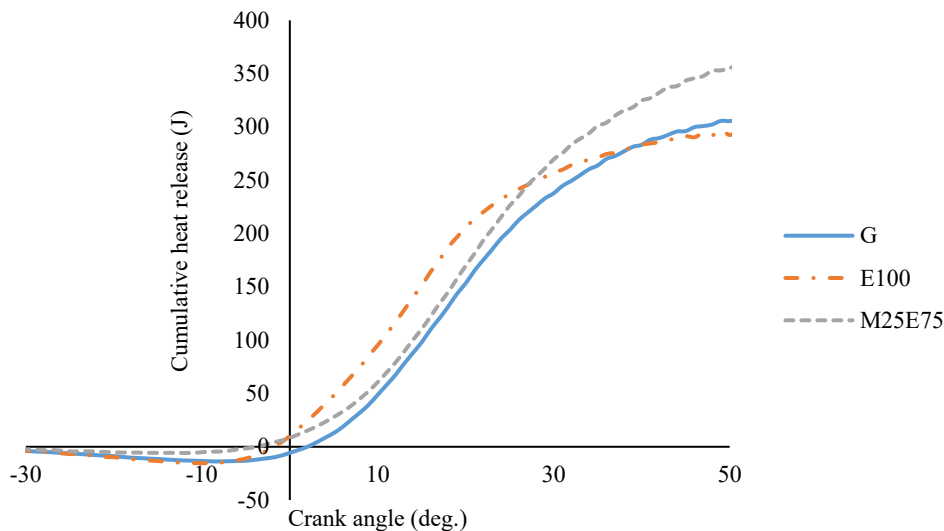


Fig. 4 Cumulative heat release at 3500 rpm

Fig. 5 indicates the combustion duration (CD) and ignition delay (ID) with the fuels at 3500 rpm. ID was almost similar with all the fuels. Combustion duration is slightly smaller by 5% with the blend as compared to gasoline. CD is the shortest with E100 which is 17.5% shorter than gasoline. Ignition delay is the period considered between spark timing and 10% mass fraction burnt. The ignition timing was advanced with the E100 and M25E75 for MBT. Alcohols have high latent heat of vaporisation and they take a longer time for evaporation than gasoline. Furthermore, ethanol (0.41 m/s) and methanol (0.43 m/s) both have higher flame speeds than gasoline (0.34 m/s) which triggered the start of combustion earlier with E100 and M25E75. Faster flame development dominated the effect of earlier ignition timing and the total duration of ignition delay with E100 and the blend happened to be almost similar to gasoline. In addition to this, during flame propagation, flame speed and rate of chemical reactions affect the combustion duration. Due to the high flame speed of ethanol combustion duration with E100 decreased.



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Cape Town, South Africa
13-15 December 2021

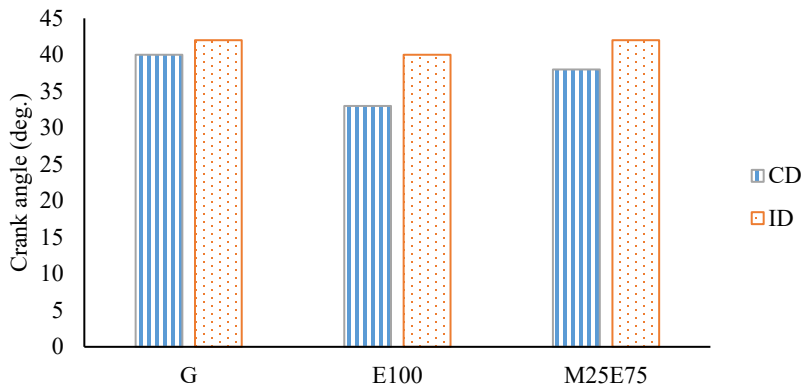


Fig. 5 Combustion duration and Ignition delay at 3500 rpm

Performance characteristics

Fig. 6 shows the brake specific fuel consumption (BSFC) of the fuels at various speeds. BSFC with E100 increased by more than 20% than gasoline at all the speeds and it reached more than 44% at 4000 rpm. In addition to this, BSFC with the blend and E100 are marginally equal. It clearly depicts that with E100 and M25E75, BSFC enhanced on account of their calorific value which is lower than gasoline. That is why at a particular load and speed, their consumption is more than gasoline. Fig. 7 indicates the brake thermal efficiency (BTE) of the engine at various speeds with E100, M25E75 and gasoline. BTE of the engine with the blend was highest among all the fuels. BTE of the engine increased by more than 25% with the blend as compared to gasoline. At 4200 rpm, it improved by 39% with M25E75 blend than gasoline. Furthermore, BTE of the engine improved by more than 22% with E100 as compared to base gasoline. At similar load and speed conditions, brake power is same for all the fuels. The difference lies in the input variable which is mass flow rate and calorific value of the fuel. Alcohols improve the mixing of charge since they are volatile in nature. It improves combustion. Combustion is better with E100 and M25E75 than gasoline. In addition to this, thermal losses from the engine are decreased on account of their high latent heat of vaporisation. Therefore, performance is also improved with these fuels. In



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



In addition to this, the brake thermal efficiency of the engine decreased at high speed with all the fuels. At higher speeds, the friction losses are higher and heat transfer loss is less. With further speed increase, friction loss dominates the decreased heat transfer loss and thermal efficiency of the engine decreases. Fig. 8 indicates the brake specific energy consumption (BSEC) of the fuels at various speeds with all the fuels. BSEC with E100 decreased by 10-23% as compared to gasoline. BSEC decreased by 18-30% with M25E75 than gasoline at various speeds. Energy consumption by E100 and the blend to achieve a particular load and speed is lower than gasoline and it is reflected through higher BTE of the engine.

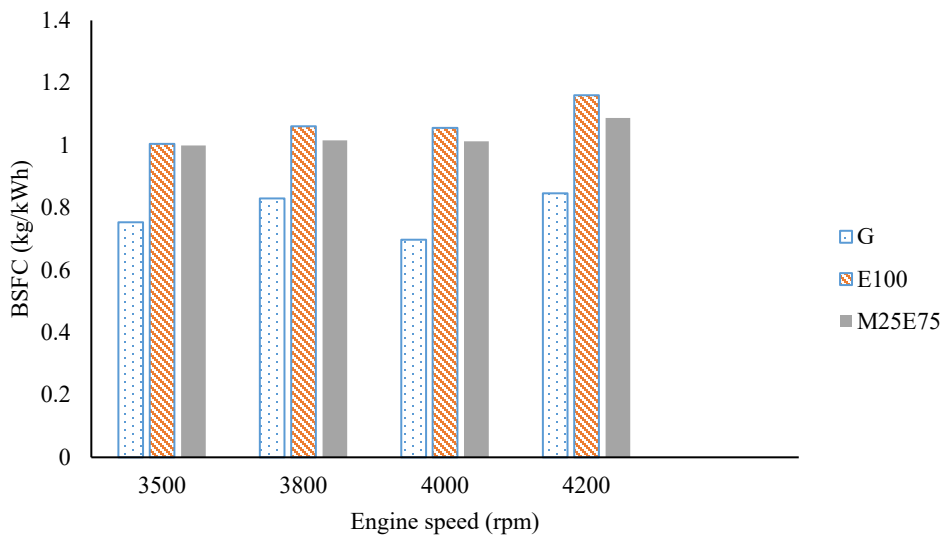


Fig. 6. Brake specific fuel consumption with the fuels



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Cape Town, South Africa
13-15 December 2021

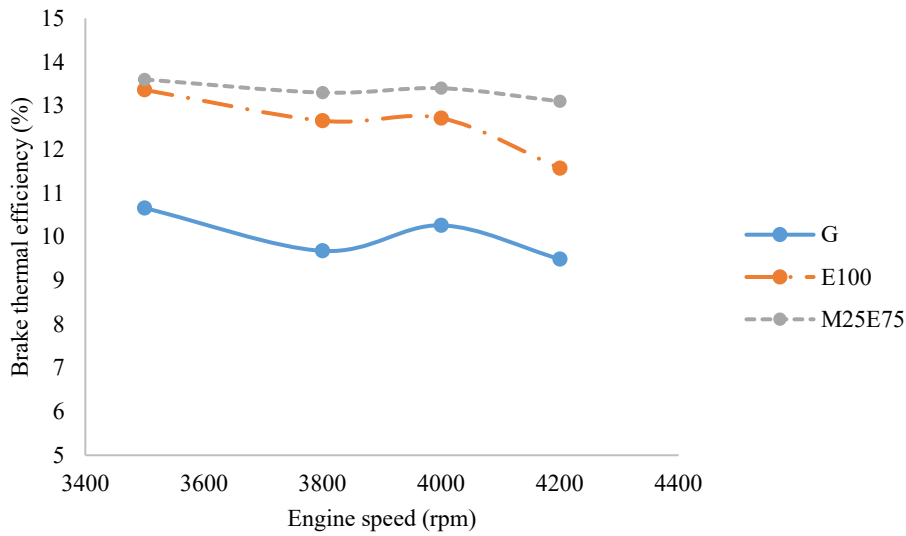


Fig. 7 Variation of brake thermal efficiency

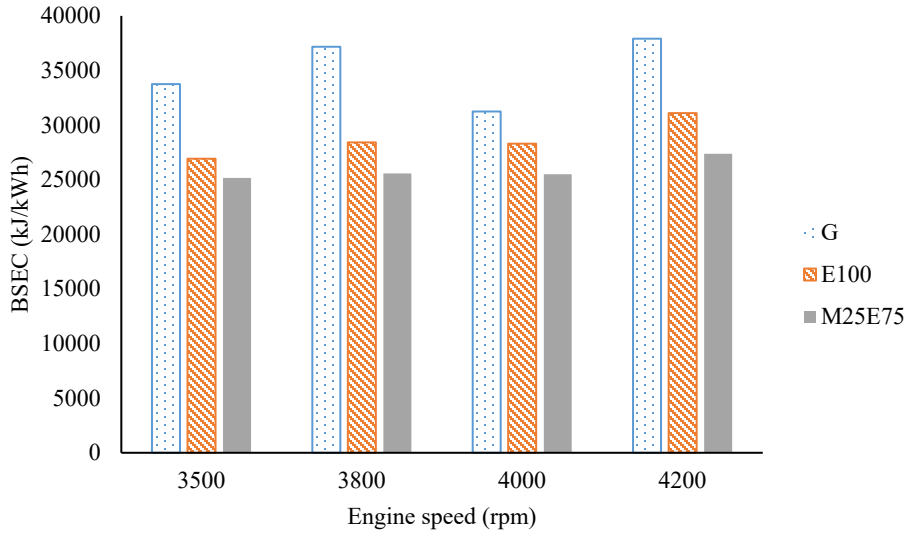


Fig. 8 Brake specific energy consumption of fuels at various speeds



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13-15 December 2021



Fig. 9 indicates the variation of volumetric efficiency of the engine with E100, M25E75 and gasoline. The volumetric efficiency increased by 6% and 24.7% at 3800 and 4200 rpm with M25E75 as compared to gasoline. A marginal increase of 3% to 11% was observed with E100. At 4200 rpm, the volumetric efficiency of the engine was nearly equal with all the fuels. Air consumption increased at 4200 rpm to meet the speed and load condition. Alcohols have high latent heat of vaporisation due to which density of incoming air decreases and more air is inducted by the engine. It improves the volumetric efficiency of the engine with E100 and M25E75.

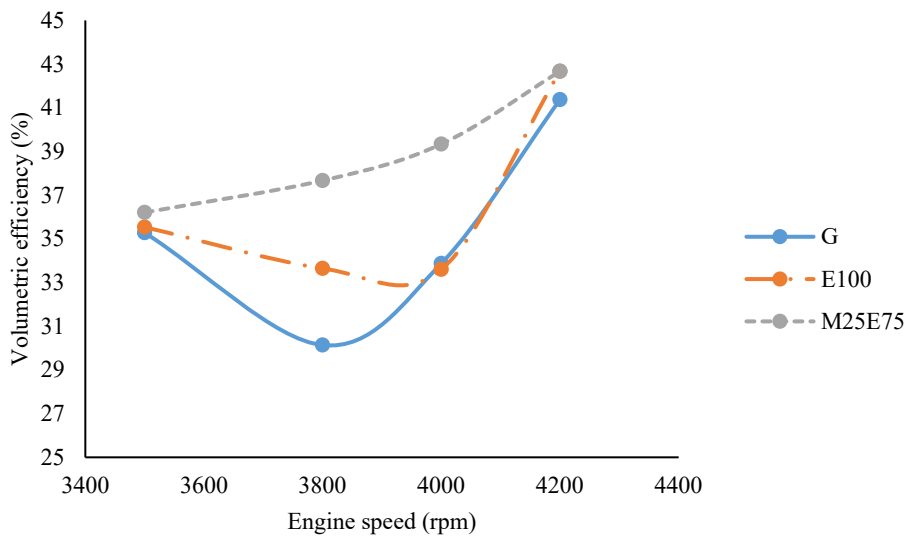


Fig. 9 Variation of volumetric efficiency with ethanol and gasoline

Emission characteristics

Fig. 10 indicates the hydrocarbon emissions at various speeds with E100, M25E75 and gasoline. HC emission increased by 1.5 times with E100 than gasoline. Various factors affect the HC emissions such as flame quenching, unburnt fuel filled in crevice volume and crankcase, less rate of oxidation during post-combustion. The latent heat of vaporisation of ethanol is higher than



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gasoline. Due to the high latent heat of vaporisation, wall quenching effect might be generated that can lead to an increase of HC emission with E100. HC emission with M25E75 and gasoline was equal at 3800 and 4000 rpm. At other speeds, it was slightly lower with M25E75 than gasoline. The presence of methanol in M25E75 could affect the HC emissions with it. The combustion pathway and intermediate products are simpler with methanol than ethanol and gasoline that can dominate and decrease the HC emission [24].

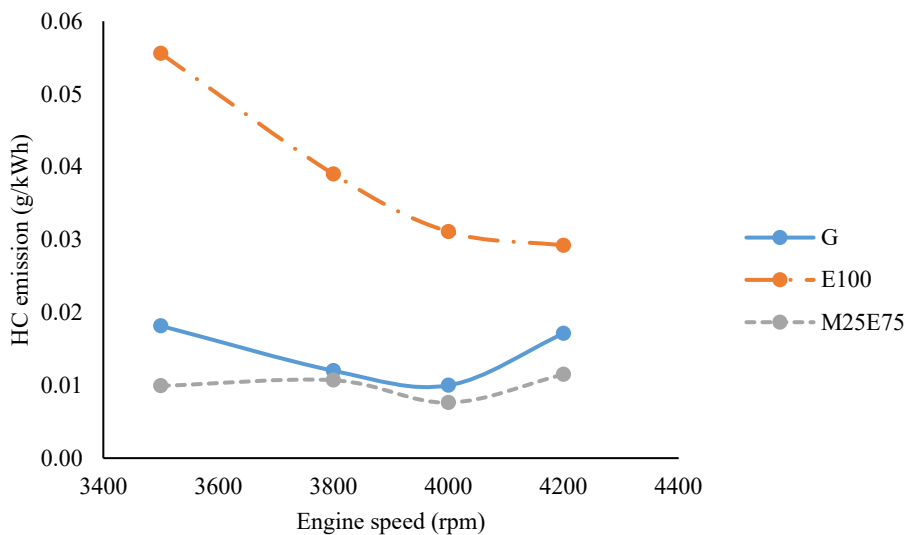


Fig. 10 Hydrocarbon emission at various speeds

Fig. 11 shows the NOx emission with both fuels. NOx emission decreased by 60-70% with E100 than gasoline. The emission decreased significantly by more than 75% with the M25E75 blend as compared to gasoline. NOx emissions are strongly affected by temperature, oxygen, and residence time. The low temperature of the combustion chamber with E100 and M25E75 is helpful in controlling NOx emission from the engine. In addition to this, NOx emission increased with speed due to less cycle time and reduced heat transfer across the cylinder wall.



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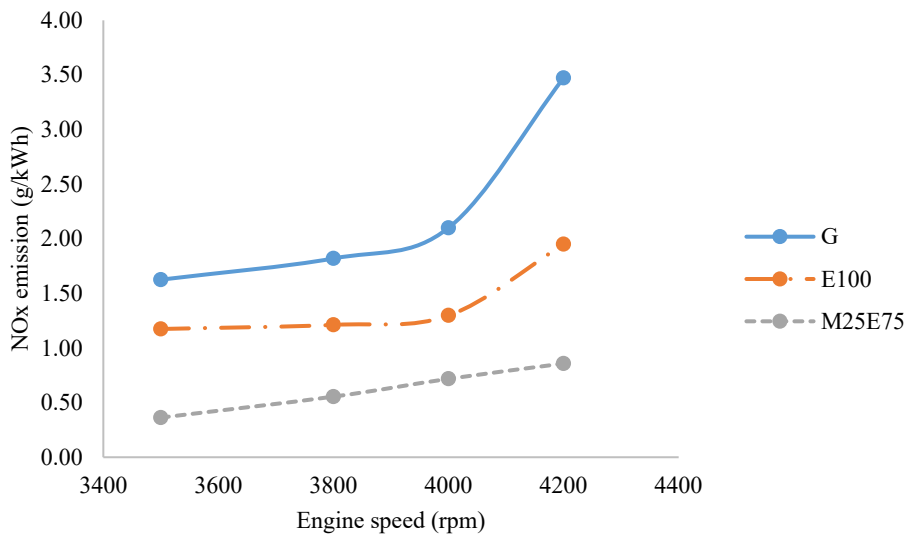


Fig. 11 NOx emission with ethanol and gasoline at various speeds

Fig. 12 shows the carbon monoxide (CO) emission with E100, M25E75 and gasoline at various engine speeds. CO emission with E100 decreased by 48% and 84% at 3800 and 4200 rpm respectively as compared to gasoline. CO emission measured with M25E75 was significantly lower by more than 80% than gasoline. Ethanol and methanol are oxygenated fuels. The molecular oxygen helps in CO conversion to carbondioxide.



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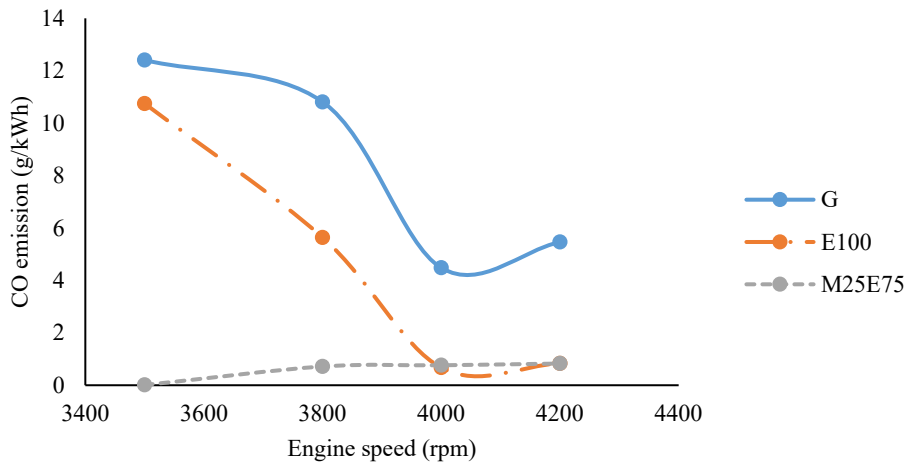


Fig. 12 Carbon monoxide emission at various speeds

Conclusions

Combustion, performance and emission characteristics of an automotive SI engine fuelled with E100 and M25E75 were compared with base gasoline at different speeds. The following conclusions are drawn from the study:

- In-cylinder peak pressure for E100 increased by 10% while with M25E75 blend, it was almost equal to gasoline. The higher flame velocity of ethanol and volatility of alcohols improve combustion and therefore peak pressure is enhanced with E100 and the blend.
- MFB profile of E100 indicated that 10% and 50% mass burnt was earlier than gasoline due to its higher flame speed. MFB profile of M25E75 blend revealed that 10% mass burnt in shorter time duration in the blend while 50% and 90% burn durations were similar to gasoline. The minimum ignition energy of methanol is very less as compared to ethanol and gasoline. It ensured a faster rate of chemical reactions and quick ignition in the blend.



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13-15 December 2021



- Ignition delay was almost similar with all the fuels. Combustion duration was slightly shorter by 5% with the blend as compared to gasoline. Combustion duration was the shortest with E100.
- BSFC with E100 increased by more than 20% than gasoline at all the speeds and increased by 44% at 4000 rpm. BSFC with the blend and E100 were marginally equal. BSFC enhanced due to lower calorific value of E100 and M25E75 blend. BSEC decreased by 10-23% and 18-30% with E100 and M25E75 as compared to gasoline at various speeds.
- BTE of the engine increased by more than 25% with the blend as compared to gasoline. At 4200 rpm, it improved by 39% with M25E75 blend than gasoline. BTE of the engine improved by more than 22% with E100 as compared to base gasoline. Ethanol and methanol are volatiles by nature which improves the mixing with air and combustion is enhanced. High latent heat of vaporisation helps in the reduction of temperature of the combustion chamber and thus thermal losses are decreased.
- The volumetric efficiency increased by 6% and 24.7% at 3800 and 4200 rpm with M25E75 as compared to gasoline. A marginal increase of 3% to 11% was observed with E100. At 4200 rpm, the volumetric efficiency of the engine was nearly equal with all the fuels. The amount of incoming air is increased with alcohols due to the cooling effect produced as a result of their high latent heat of vaporisation.
- HC emission increased by 1.5 times with E100 than gasoline due to enhanced flame quenching as a result of the cooling effect produced by E100. HC emission with M25E75 blend was slightly equal with gasoline. The presence of methanol in the blend influenced the HC emissions. The combustion pathway and the intermediate products produced during its combustion are simpler than E100 and gasoline.
- NO_x emission decreased by 60-70% with E100 than gasoline. The emission decreased significantly by more than 75% with M25E75 blend as compared to gasoline. The low



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Cape Town, South Africa
13-15 December 2021



temperature of the combustion chamber with E100 and M25E75 is helpful in controlling NOx emission from the engine.

- CO emission with E100 decreased by 48% and 84% at 3800 and 4200 rpm respectively as compared to gasoline. CO emission measured with M25E75 was significantly lower by more than 80% than gasoline. Molecular oxygen which presents in E100, and the blend, helps in the conversion of CO to CO₂.

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IMPACT OF LIFE CYCLE ASSESSMENT FOR MUNICIPAL PLASTIC WASTE TREATMENT IN SOUTH AFRICA

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ABSTRACT

Municipal Plastic Wastes (MPW) can have a number of negative effects on the environment and this is causing a growing concern which requires urgent intervention. Addressing this environmental challenges by proffering alternative end-of-life (EOL) techniques for MPW treatment is thus critical for designing and implementing effective long-term remedies. In this study, the environmental implications of several MPW treatment technologies were assessed using life cycle assessment (LCA). Our focus was on four potential waste treatment scenarios for MPW: waste disposal via landfill, waste incineration, waste regeneration, and reusability of recycled waste. The findings show that recycling has a greater benefit over landfilling and incineration methods.

The most important environmental benefit comes from the recycling of plastics, which may serve as good source materials for environmental friendly products. Following a holistic evaluation, five major factors that influence the overall impact on the environment were outlined: the mass fraction in waste, the recycling rate, the conversion efficiency, the waste-to-energy conversion rate, and the type of energy which can be utilized from incineration generated energy.

Key words: Municipal plastic waste, Life cycle assessment, waste-to-energy, End-of-Life, Incineration, Recycling, Landfill.



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INTRODUCTION

Both policymakers and the general public have been paying close attention to the issue of plastic waste in recent years. Plastic waste frequently enters the environment (either as litter or as a result of waste management system leakage), where it degrades slowly, usually decomposing physically into micro-plastic particles, possibly contaminating land based, oceanic, and underwater ecosystems and putting living creatures at risk (Russo et al., 2020)

As shown in the 2018 State of Waste Report, South Africa produced 55 million metric tonnes of municipal solid wastes in 2017, with 25% of that being plastic waste and just 11% being diverted from landfill. Increases in waste creation are linked to these trends, which are accompanied by slow growth in the Gross Domestic Product (GDP) (Russo et al., 2020).

Plastic waste generation on such a large scale has a major negative influence on the environment. Plastic waste is swallowed-up by 44 percent of seabird species once it enters the coastal ecosystems, and plastic waste affects at least 267 species of marine creatures globally including South Africa (Moore, 2018).

Generally, the majority of plastic waste is discarded of in the same manner as other municipal waste. Landfilling, the traditional method for disposing of municipal waste, takes up a lot of area but has been recognized as one of the primary sources of greenhouse gases that cause global warming (Kumar et al., 2014). Incineration eliminates waste disposal in landfills and allows for the recovery of energy. Incineration, on the other hand, produces and releases contaminants (Wiles, 2016). Conversely, recycling is well-known for its environmental advantages, since it allows plastic waste products to be reprocessed. Composite timber, boxes, and bags may all be made from recycled plastic waste (The Association of Plastic Recyclers, 2018). Furthermore, collecting and transporting recyclable materials consumes energy and resources, the quantities of which vary and



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depend on the location and kind of waste. In light of these factors, a study of the environmental costs and advantages of different end-of-life treatments for plastic waste is provided here.

The life cycle assessment (LCA) technique is used to evaluate a product's or process's cumulative environmental effect over its entire life cycle, including resource extraction, materials processing, manufacture, transportation, usage, and end-of-life disposal. LCA may assist drive policy and technological development by including all phases of a product's life cycle and a wide variety of environmental consequences. This can help minimize environmental burden shifting between various stages and types of impacts. Molgaard, 2015; Barton et al., 2016; Craighill and Powell, 2016) have all done LCA analyses on waste management techniques throughout the millennium. When it comes to life cycle energy usage and global warming potential, Björklund and Finnveden (2015) analyzed 40 LCA case studies and discovered that recycling is, in most circumstances, superior to landfilling or incineration. Laurent et al. (2014) looked at 222 LCA studies of municipal solid waste management systems and found that the LCA findings are heavily influenced by native features.

Material and Methods

This research was carried out in accordance with the ISO14040/14044 LCA process standard (ISO, 2016). This study overall aim is to examine the environmental impacts of various end-of-life treatments for post-consumer plastic waste over their entire life cycle, with a specific goal of evaluating and comparing the environmental impacts of different end-of-life procedures under various collection and waste mixture occurrences.

The plastic waste included within one metric ton of recyclable waste or mixed waste has been chosen as the functional unit. According to Pressley et al. (2015), the bulk proportion of plastic waste in recyclable waste and mixed waste is 0.6 percent and 2 percent, respectively.



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From post-use until end-of-life, the system boundary is established (as shown in Figure 1). The plastic waste from a product sold is dumped into either a mixed waste or a recyclable waste stream after it has been utilized. Trucks pick up mixed waste and transport it to a landfill, an incinerator for energy recovery, or a materials recovery facility (MRF) for recycling. Refuse vans fetch recyclable waste or users drop it off at designated collection places, and it is subsequently transported to an MRF for recycling. Recycled leftovers are disposed of in landfills or incinerators for energy conversion. Listed below are the four scenarios explored:

- ❖ Landfill disposal of plastic waste in mixed waste;
- ❖ Combustion of plastic pollution in mixed waste;
- ❖ Regeneration of plastic in mixed waste; and
- ❖ Recovery of waste plastics in biodegradable material

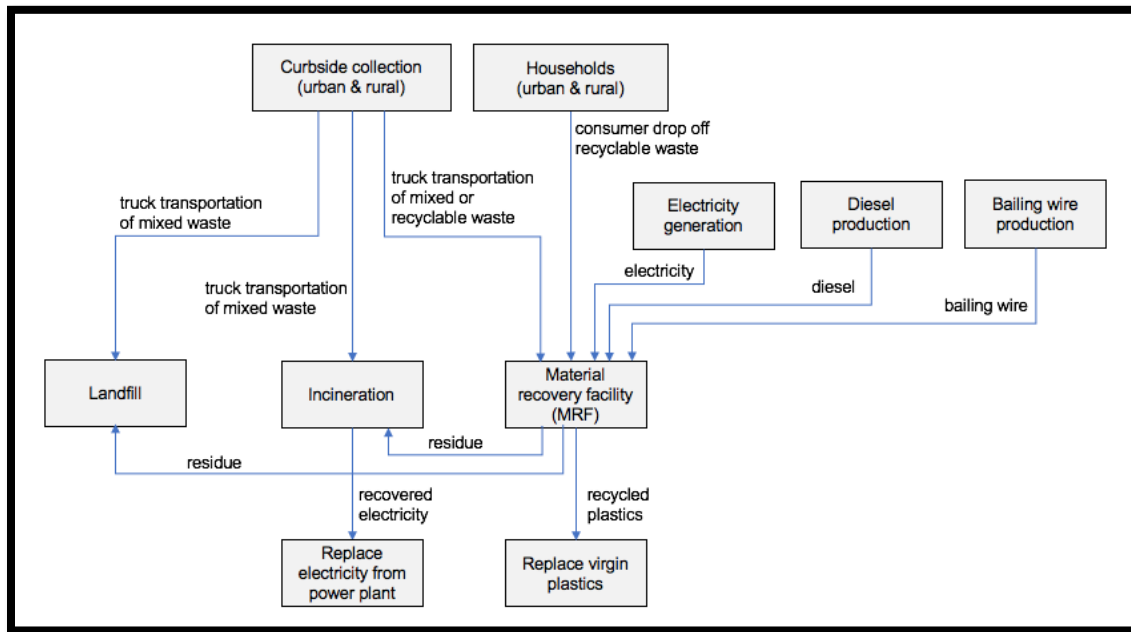


Figure 1. Process flow diagram of the post-consumer plastic film treatment system.

Inventory analysis of the entire product lifecycle



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The mass and energy intake, as well as the produced emission, of a product system are quantified in a life cycle inventory (LCI) study. The majority of the data on relevant activities in this analysis, such as plastic waste collected and treated from landfill, incineration, or recycling, came from peer-reviewed, published studies. When particular data is described, it is referenced.

Gathering of the Municipal plastic wastes

The plastic waste collection distance comprises the distance traveled by the collection vehicle from the facility parking lot to the location where the waste is offloaded (e.g., an MRF or incineration site), and back to the parking. The collection distances for recyclable and mixed waste for typical metropolitan areas in the South Africa are shown in Table 1. According to Nguyen and Wilson (2020), a kilogram of waste pickup in rural regions needs 5 to 6 times the amount of gasoline as an urban route.

As a result, increasing the collection distance for the urban route by a factor of 6 yields the collection distance for the rural situation. Because the amount of recyclable plastic waste collected each route is lower, the collection distance for recyclable waste is longer on a unit mass basis than for mixed waste. The collection distance refers to the distance traveled per collection trip, which is then multiplied by the collected waste mass per trip to get the total distance traveled for collecting per functional unit waste. The distance to transport the plastic waste is then determined by multiplying the mass fraction in recyclable or mixed waste (0.6 percent and 2 percent, accordingly) by the distance (Table 2). To evaluate the environmental effect of waste collection by trucks for mixed and recyclable waste, the EcoInvent 2.2 for truck transport of municipal waste was utilized (EcoInvent, 2020). The SimaPro 8.4 LCA software environment was used to create process models and life cycle inventory for various plastic waste treatment scenarios after all unit process data has been gathered (Pre Consultants, 2019).



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Material Recovery Facility (MRF)

The reusable component of plastic waste collected and delivered to an MRF are separated and processed. Table 3 shows how much energy and materials an MRF uses to treat one metric ton of plastic waste. Table 4 illustrates the associated energy and material usage, as well as their distribution to the waste stream's component based on their mass ratio. These figures are for mechanical separation, which is the most common method of recycling at an MRF. (Testin and Vergano,2017).

Incineration

The produced char can be transported to incinerators for waste heat recovery. Mixed waste has a residue percentage of 76%, whereas recyclable waste has a residue rate of 10%. (Pressley et al., 2015). The focus here is on recovery of energy from the combustion of plastic wastes. The plastic waste composition of the residue provided for incineration, as well as the heating value of each type of polymer, are listed in Table 5. Wollny et al. (2018) estimated the quantity of energy created by the conversion of these polymers using an energy conversion efficiency of 7.7%. The unit process data for incineration is derived from the electricity recovered, the mass fraction of the plastic waste, and the residual rate (Table 6). The incineration records in the EcoInvent 2.2 database are used to describe the emission of harmful chemicals such as dioxins from incineration (EcoInvent, 2020).

Landfill Site

Residues produced from MRF and collected mixed waste can be transported to landfill as a potential substitute to incineration. The weight ratio of plastic waste deposited in a landfill corresponds to its weight fractions in mixed waste. The quantity of waste transferred to landfills



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in MRF residues is determined by multiplying the residual rate of mixed or recyclable waste by the weight fractions of plastic wastes in the waste stream (Table 7).

Results

Initial considerations include five waste collection scenarios and four MRF residue treatment scenarios. The life cycle consequences of landfill disposal, incineration, and recycling of plastic waste are then calculated using the corresponding "worst-case" scenarios for combined waste and recycled products as extremely rough estimates.

Evaluation of waste collected scenario

A comparison of the five collecting contexts is shown in Figure 2. Consumer drop-off has the greatest environmental effect of these instances. Reason is because a passenger car can only transport a fraction of the waste that a truck can, more trips are then required to gather similar amount of waste. The principal environmental impacts attributed to collection are global warming from carbon dioxide emissions during truck transportation; smog, from nitrogen oxides and particulate matters emissions; and natural resource depletion due to crude oil-based fuel consumption.



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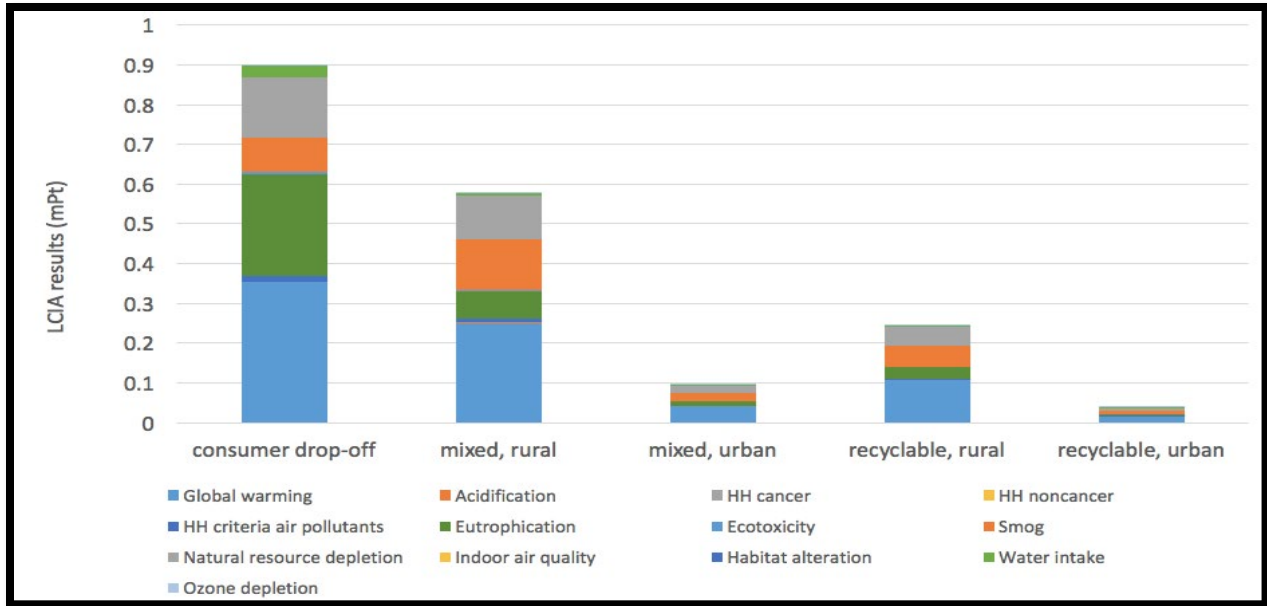


Figure 2: Environmental impacts of different collection scenarios.

In Figure 3, evaluation of the life cycle implication as relates to landfilling, incineration, and recycling of plastic waste in mixed and reusable waste streams were examined. The findings show that recycling mixed or recycling plastic waste is better for the environment than either direct incineration or landfill disposal of mixed waste. Because the weight percentage of plastic waste in mixed waste is higher than in recyclable waste, indicating that mixed waste recycling provides a greater value than recycling of “recyclable” waste.



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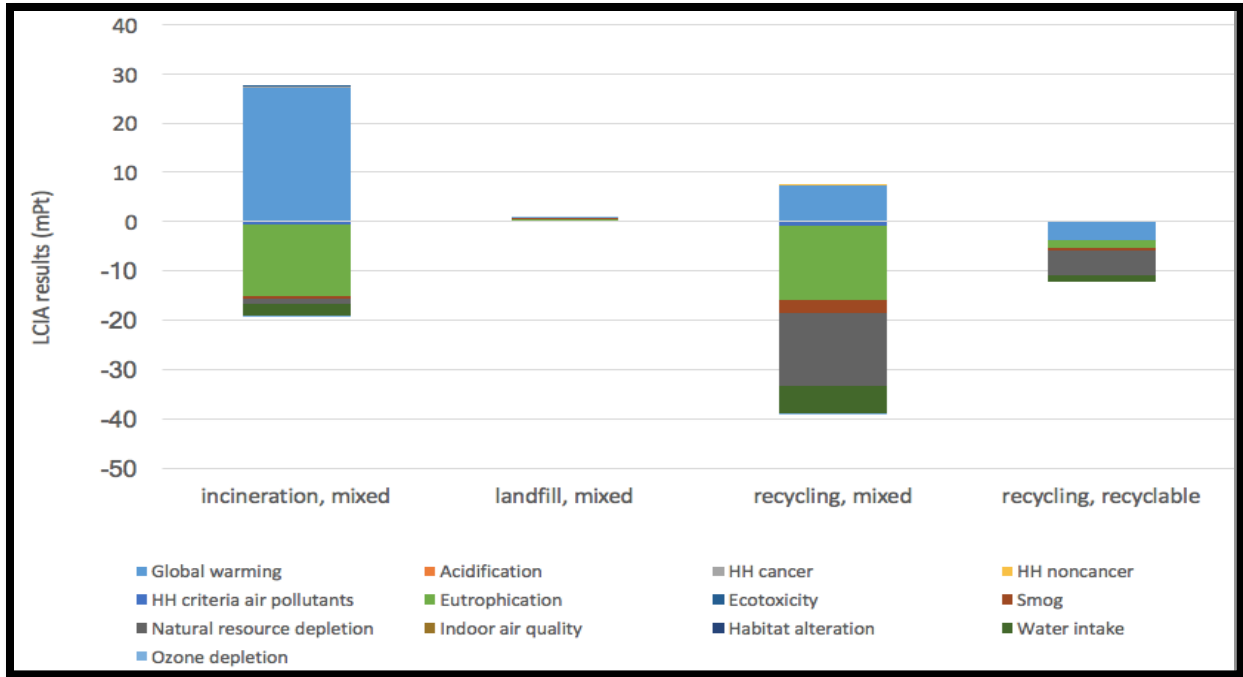


Figure 3: Environmental impacts of different plastic waste end-of-life treatment scenarios.

Conclusions

According to the results of the life cycle analysis done in this study, recycling plastic waste has an environmental benefit over landfilling or incineration.

Recycling tends to be highly advantageous when the plastic waste is recovered from mixed waste rather than recyclable waste and this due to its volume ratio in mixed waste despite its lower recyclable performance. However, it does not indicate that recycling from recyclable plastic waste should be discouraged rather, it is about the method of managing the waste. Therefore, government regulations should encourage consumers to segregate plastic waste from mixed waste in order to improve the proportion of polyesters that can be recovered from recyclable waste.



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Since there are considerable benefits to recycling plastic waste, more efforts should be devoted to increasing the total recycling rate. Waste recycling still faces technical challenges. This process requires specialized equipment. However, a substantial volume of plastic waste is necessary to make the equipment investment economically viable. To begin, packaging manufacturers should create simple and easy degradability tags that provide required information, such as how to keep the plastic dry and clean and where to dispose it. Secondly, local municipalities should work with industry professionals to educate citizens about plastic waste recycling and urge them to participate. Furthermore, public financing is necessary until the amount of recycled waste is significant enough to make recycling economical.

Acknowledgment: The authors would like to express their gratitude to the National Research Fund (NRF) of South Africa and the Durban University of Technology for their financial support.

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APPENDIX

TABLE 1: Transportation data for collecting one metric ton of waste

Parameters	Mixed waste, urban	Mixed waste, rural	Recyclable waste, urban	Recyclable waste, rural	Consumer drop-off	Unit	Data source
Distance between collection route and destination	30	130	45	218	N/A	km	Data for mixed and recyclable waste is from Jaunich et al., 2016; Data for consumer drop-off is from MSW-DST and Franklin associates, 2019
Distance between destination and parking	6.7	166	50	251	N/A	km	
Distance between parking and collection route	53	38	3.6	21	N/A	km	
Total distance	56	329	79	483	17.5	km	
Waste mass per trip	31	31	31	28	0.015	t	



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TABLE 2: Unit process data for collecting one metric ton of film waste.

Materials	Mixed, urban	Mixed, rural	Recyclable, urban	Recyclable, rural	Consumer drop-off	Unit	Upstream processes
Truck transportation	0.05	0.35	0.05	0.16	N/A	tkm	Transport, municipal waste collection, lorry 21t/CH S
Consumer transportation	N/A	N/A	N/A	N/A	3.6	km	Transport, passenger car {RoW} market for Alloc Def, S

TABLE 3: Energy and material consumption at a MRF for one metric ton waste.

Parameters	Mixed waste	Recyclable waste	Unit	Data Source
Electricity	7.9	6.3	kmh	Pressley et al., 2015
Diesel	0.7	0.7	L	
Bailing wire	0.8	0.4	kg	

TABLE 4: Unit process data for MRF for disposal of one metric ton of film waste.

Materials	Mixed waste	Recyclable waste	Unit	Upstream processes
Electricity	0.17	0.39	kmh	Electricity, at grid,
Diesel	0.58	0.16	L	Diesel, combusted in industrial equipment
Bailing wire	0.012	0.018	kg	Steel, unalloyed {GLO} market for Alloc Def, S



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13-15 December 2021



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TABLE 5: Energy generated from combustion of one metric ton of plastic film waste.

Polymer	Portion of plastic waste (%)	Lower heating value (MJ/ton)	Energy generated (KJ)
LDPE	68.9	44.3	30500
HDPE	6.8	44.3	3030
PET	12.1	23.9	2900
PP	8.5	44.3	3750
PVC	3.1	19.2	600
PS	0.5	41.5	216
TOTAL	100	-	41000

TABLE 6: Unit process data of incineration for disposal of one metric ton of waste.

Materials	Directly incinerated after collection (mixed waste)	Incineration after recycling at MRF		Unit	Upstream processes
		Mixed waste	Recycle waste		
PE (LDPE & HDPE)	15.1	11.5	0.45	kg	Disposal, polyethylene, 0.4% water, to municipal incineration/CH S
PET	2.4	1.8	0.07	kg	Disposal, polyethylene terephthalate, 0.2% water, to municipal incineration/CH S
PP	1.7	1.3	0.05	kg	Disposal, polypropylene, 15.9% water, to municipal incineration/CH S
PVC	0.62	0.48	0.02	kg	Disposal, polyvinylchloride, 0.2% water, to municipal incineration/CH S
PS	0.10	0.08	0.003	kg	Disposal, polystyrene, 0.2% water, to municipal incineration/CH S
Energy recovered	-64.6	-48	-1.9	MJ	Electricity, production mix SA/SA S



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13-15 December 2021



TABLE 7: Unit process data for landfilling one metric ton of waste.

Materials	Directly sent to landfill after collection (mixed waste)	Landfill disposal of residues after recycling at MRF		Unit	Upstream processes
		Mixed waste	Recycle waste		
Landfill waste	20	18.2	0.5	kg	Disposal, plastic plaster, 0% water, to inert material landfill/CH S



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Cape Town, South Africa
13-15 December 2021



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CO-GASIFICATION OF BIOMASS AND PLASTIC WASTE: A MINI REVIEW

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Abstract-The interest in gasification has been growing globally due to the need for; alternative energy recovery technologies, cleaner energy sources and sustainable methods of managing waste which do not negatively impact human health and the environment. The aim of this paper was to determine the effect of co-gasifying biomass and plastic wastes by reviewing the existing body of literature. The key findings are that; co-gasification of biomass and plastic wastes has the potential to transform the energy and waste management sectors in South Africa by providing an alternative cleaner fuel and stamping out the tide of plastic waste simultaneously. Co-gasification of these feedstocks will also ensure a constant supply of feed especially in seasons where biomass feedstock levels may be low. The positive synergistic effects observed in the various reviewed studies warrant further investigation into the suitability of this process in the South African context.

Keywords- Biomass; Co-gasification; Plastic waste; Synthesis gas



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13-15 December 2021



1.0 INTRODUCTION

The interest in gasification has been growing globally due to the need for; alternative energy recovery technologies, cleaner energy sources and sustainable methods of managing waste which do not negatively impact human health and the environment. Gasification is a thermochemical process, in which carbon-based compounds are converted into a gas referred to as synthesis gas (syngas) in the presence of limited oxygen, air, water vapour or carbon dioxide (CO₂). The syngas mainly consists of carbon monoxide (CO), hydrogen (H₂), methane (CH₄) and CO₂. However, it may also contain nitrogen (N₂). (Abubackar et al., 2019).

Biomass and post-consumer plastic wastes are among some of the alternative energy sources to coal that have been widely researched together with gasification technology (Pinto et al., 2002). In comparison to other thermochemical processes such as pyrolysis, liquefaction and combustion; gasification and pyrolysis are reportedly most effective in generating valuable products from biomass (Fan et al., 2019). Syngas can be used to produce heat and/or electricity in combined heat and power plants or as a feedstock in other chemical processes such as Fisher–Tropsch process or in the production of chemicals including methanol, dimethyl ether, and ammonia (Brachi et al., 2014). Production of bio-methanol is also advantageous in that; fossil fuels normally used are preserved while high amounts of green-house gases associated with these fuels are also prevented (Brachi et al., 2014). The syngas composition is determined by; feedstock composition, process



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Cape Town, South Africa
13-15 December 2021



parameters, gasifying medium, and type of gasifier used (Abubackar et al., 2019) (Brachi et al., 2014).

Other by-products of the process include ash, char, tar, acetylene (C_2H_2), ethylene (C_2H_4), propane (C_3H_8), ammonia (NH_3), nitrogen and sulphur oxide gases (NO_x and Sox) and phenols. During gasification, there is a possibility of lignocellulosic material being converted into syngas completely. The energy from biomass which is utilised by living organisms is derived from the sun and then stored as chemical energy. Globally, an estimated 100 billion tonnes per year of biomass are produced and being in fourth position, biomass is among the leading energy sources. The advantages of biomass are that it; is a renewable source of energy, generates low emissions, therefore cleaner and is abundant (Fan et al., 2019) . Thus, to preserve depleting non-renewable resources, as well as minimise adverse impacts on the environment, biomass beneficiation should be explored. This renewable material has also been touted as a viable source of hydrogen through gasification and pyrolysis although low recoveries between 5 to 8% currently make the process unattractive. Traditionally, hydrogen is produced from; fossil fuels, electrolysis of water, photolysis or thermolysis (Alvarez et al., 2014) and can be utilised to generate electricity or as a transportation fuel (Alvarez et al., 2014).

Various researchers have undertaken studies to assess the quality of products generated from biomass gasification. The high content of oxygen in generated products reduces calorific value



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Cape Town, South Africa
13-15 December 2021



and stability under heat stress which consequently limits its areas of application (Król-Morkisz & Pielichowska, 2019). Moreover, biomass is seasonal and therefore to prevent supply challenges and enable continuity of the process, supplementing with alternative feedstock is necessary (Pinto et al., 2002) (Lopez et al., 2015). Biomass also has a low calorific value which is less than 8000 MJ/m³ and the costs associated with bio-methanol production are reportedly 1.5 to 4 times higher than those from natural gas due to the contaminated syngas from biomass (Brachi et al., 2014). Co-gasification with plastic waste may also reduce these costs and make the process financially feasible.

This paper aims to; determine the effect of co-gasifying biomass and plastic waste by reviewing the existing body of literature, determine suitable gasification technology that can be used, determine the operating conditions for the co-gasification process and determine the various co-gasification media that can be used.

2.0 DATA SOURCES

Peer-reviewed literature was accessed from various academic databases including Web of Science, Google Scholar and Scopus. Some of the key words/phrases used individually and in combination were gasification of plastic waste, gasification of biomass, co-gasification of biomass, gasification



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Cape Town, South Africa
13-15 December 2021



technology, co-gasification operating conditions, life cycle analyses. Only review and research articles between 2000 to 2021 written in English were considered.

3.0 LITERATURE REVIEW

There are many perceived benefits of waste co-gasification that have been reported and these include ability to gasify several wastes at the same time, thereby reducing costs associated with separation of wastes as well as increased plant availability which is not subject to seasonal variations in biomass feedstock. The products produced from co-gasification or co-pyrolysis of biomass with plastic waste reportedly contain less oxygen and therefore are of improved quality. This is attributed to the high hydrogen content and low oxygen content in plastics such as polyethylene (PE), polystyrene (PS), polypropylene (PP) and polyethylene terephthalate (PET) (Fan et al., 2019). Values as low as 0% oxygen have been reported for high density polyethylene (HDPE) compared to 44.5% for biomass (Lopez et al., 2015).

The availability of huge amounts of feedstocks also enables building of large plants which in turn aids the economics and control of the process while alkali metals in biomass improve the reaction kinetics of the gasification process (Lopez et al., 2015). Plastic waste addition also prevents the generation of significant amounts of tar which is characteristic of pure biomass steam gasification while biomass also; prevents the feeding challenges associated with plastic waste as it softens on



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Cape Town, South Africa
13-15 December 2021



exposure to heat and sticks to the reactor walls as well as generation of fine char which reportedly can remain in the reactor, cyclone and condenser (Pinto et al., 2002).

(Lopez et al., 2015). Biomass also lowers the temperature at which the plastic waste decomposes, which in turn improves liquid yield (Alvarez et al., 2014). Furthermore, noting the benefits associated with hydrogen, it is reported that co-gasifying biomass and plastic such as polyethylene (PE), polypropylene (PP) and polystyrene (PS) wastes increases the amount of hydrogen that can be produced (Alvarez et al., 2014) thereby providing a sustainable alternative to fossil fuels. Table 1 shows some of the co-gasification studies reviewed in this work.

4.0 DISCUSSION

F. 4.1 Operating conditions

There exists an untapped opportunity in the field of co-gasification of plastic wastes and biomass. In the reviewed studies, operating temperatures were generally between 800 to 900 °C while steam, oxygen, air and carbon dioxide were some of the gasification media used. Single and two stage reactors used included fluidised bed, downdraft, conical spouted bed and fixed bed reactors. Lopez et al. (Lopez et al., 2015) cites Arena et al. (Arena, 2011) who reviewed various studies which recommended the use of a conical spouted bed reactor for feedstocks of variable density and particle size as bed fluidity is not compromised due to the design of the reactor; specifically the spouted section. Moreover, in this type of reactor, particle segregation is minimal, there is excellent



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13-15 December 2021



mixing and good heat transfer, low pressure drop across the bed and a reduced quantity of the fluidising media is required. Alvarez et al. (Alvarez et al., 2014) recommend the use of two stage reactors in order to improve gas yield. Catalysts that have been recommended to reduce tar formation include; dolomite and olivine (Lopez et al., 2015).

G. 4.2 Benefits of co-gasification

Plastic waste in co-gasification with biomass increases; the yield and quality of the synthesis gas or oil produced and the reactivity of the plastic/wood mixture. The increase in syngas quality is attributed to the increase in gases such as hydrogen and methane and a corresponding decrease in carbon dioxide which in turn improves the calorific value of the produced syngas. The ability to co-gasify various wastes also increases the availability of feedstock needed for the process (Alvarez et al., 2014) (Lopez et al., 2015) (Brachi et al., 2014) while biomass presence in plastic waste gasification reduces operational challenges during feeding.

H. 4.3 Potential problems associated with biomass gasification

Despite these perceived benefits of co-gasification, using chemically treated woody biomass may have significantly higher negative environmental impacts compared to gasification of pure polyolefins. An example is chromated copper arsenate (CCA), a wood preservative used on outdoor wood, which releases toxins when burnt that can cause lung cancer (Greater Wellington



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Regional Council, n.d.). Furthermore, the energy requirements of the process may be higher with biomass gasification.

5.0 CONCLUSION

Co-gasification of biomass and plastic wastes has the potential to transform the energy and waste management sectors in South Africa by producing an alternative cleaner fuel and stamping out the tide of plastic waste simultaneously. Co-gasification of these feedstocks will also ensure a constant supply of feed especially in seasons where biomass feedstock levels may be low. The positive synergistic effects observed in the various reviewed studies warrant further investigation into the suitability of this method in the South African context.

ACKNOWLEDGEMENT

The authors would like to thank the University of Johannesburg and the Botswana International University of Science and Technology for provision of funding.

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1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



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Cape Town, South Africa
13-15 December 2021



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Cape Town, South Africa
13-15 December 2021



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Cape Town, South Africa
13-15 December 2021



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Table 1. Co-gasification studies involving biomass and plastic waste (generated by authors)

Country, Author	Plastic	Biomass source	Operating conditions	Technology used	Media	Comments
China, (Fan et al., 2019)	HDPE	Eucalyptus wood, rice straw	Drying at 105 °C Reaction stages-biomass decomposition, PE degradation, reaction of CO ₂ with products (200->700 °C) Max. temperature: 1 000 °C Biomass: HDPE ratio – 1:1	Thermogravimetry with a Fourier transform infrared spectrometer (TG-FTIR)	CO ₂ at 20l/min	More oxygen, Na, K, Ca in solid residues than for pure biomass. More carbon and less oxygen content in volatile products. Less CH ₄ and CO produced while generation of H ₂ O increases.
Spain, (Lopez et al., 2015)	HDPE		900 °C Ratio of steam/(biomass + plastic) = 1 Olivine catalyst to reduce tar formation	Conical spouted bed	Steam	Tar and char reduced. Tar in gas reducing by 83% compared to pure biomass gasification for a biomass: HDPE ratio of 1: 1.
Portugal, (Pinto et al., 2002)	PE	Pine	N ₂ used as a carrier gas, 730-900°C, steam/waste ratio between 0.4–0.9, feed flowrate was 5.7–12.5 g/min, particle size between 1250–2000 µm.	Fluidised bed	Steam at 5.3 g/min	Substitution of biomass with plastic waste up to 60% is possible. More H ₂ than CO is produced when PE is introduced.



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Cape Town, South Africa
13-15 December 2021



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						Highest gas yield was reached at 60% PE (w/w).
Spain, Japan, UK (Alvarez et al., 2014)	PP, PS, HDPE	Sawdust	600 °C in the pyrolysis zone at a heating rate of 40 °C/min, 900 °C in the gasification zone.	2 stage fixed bed reactor	Steam, H ₂ O injection at 4.74 ml/ hr	Plastic waste addition increased gas yield & H ₂ production, more so with PP than PS. CO and CO ₂ reduced.
Slovenia, (Narobe et al., 2014)	PE	Wood pellets	Mass ratio of steam-to-carbon was 2.3 850 °C	Fluidised bed	Steam	Feeding directly onto the bed reduces tar formation CO ₂ content is minimised when plastic content increases; due to the reduced decarboxylation reactions which are common with biomass.
China, (Wang et al., 2021)	PET, HDPE	Pinewood pellets	800 °C	Fixed bed reactor	CO ₂	Softened PET reduced biomass porosity. HDPE appeared more beneficial than PET in co-gasification.
America, (Ahmed et al., 2010)	PE	Wood chips	900°C	Semi-batch reactor	Steam	Synergistic effects were observed. There was an improvement in gas, H ₂ , total hydrocarbons, and energy yield including thermal efficiency.



1st Sustainable Bioenergy and Processes Conference

Cape Town, South Africa
13-15 December 2021



Malaysia, (Basha et al., 2020)	PS	Palm kernel shell	800 °C, 900 °C	Electrical downdraft reactor	Air	At 900 °C, yield of syngas was high but decreased at 800 °C with increase in PS.
Republic of Korea & Saudi Arabia, (Park et al., 2016)	HDPE	Wood pellets	526 °C, 626 °C	2 stage gasifier (oxidative pyrolyser/ thermal plasma reactor	Oxygen, steam	As HDPE content increased, CH ₄ and hydrocarbon yields also increased. CO ₂ yield increased with increasing biomass concentration.
America, (Burra & Gupta, 2018)	PC, PE, PP	Pine wood	900 °C	Semi-batch reactor	Steam	Increase in syngas yield and quality.



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Cape Town, South Africa
13-15 December 2021



Application of Biofuels in Automotive Vehicles

Prof. K. A. Subramanian, Head & Professor, Department of Energy Science and Engineering, IIT Delhi,

New Delhi - India Abstract:

The utilization of Biofuels in automotive engines/vehicles is imperative to achieve a part of the sustainable goal of net zero-emission by the year 2050. Biofuel is carbon-neutral fuel as well as a carbon sink. The road transport sector accounts for 17% of global greenhouse gas emissions (UNFCCC). The potential biomass feedstock includes agricultural residue, forest wastes, energy crop products, industrial waste, municipal solid waste, etc., producing biofuels. In addition, Biofuels provides to increase energy security, enhance fuel quality, reduce regulated and GHGs emissions, increase fuel economy with tangible benefits, including expansion of habitat and food web, improving soil quality, preventing soil erosion, and oxygen generation. Biofuels such as methanol (CH_3OH), Ethanol ($\text{C}_2\text{H}_5\text{OH}$), biomethane (CH_4), biodiesel, dimethyl ether ($\text{CH}_3\text{-O-CH}_3$), Fisher-Tropic Diesel (C_xH_y), and Bio-hydrogen (H_2) are derived from the biomass through biological/thermochemical conversion processes. Biofuel generally has lower sulfur content resulting in negligible SO_x emission from combustion engines. Biofuels have higher octane numbers (100 (Methanol), 100 (Ethanol), 110 (biomethane), 120 and above (biohydrogen)) and higher cetane numbers (58 (Biodiesel), 58 (Dimethyl ether), 75 (Fisher-Tropsch Diesel)) compared to gasoline (95 Octane Number) and diesel (51 Cetane Number). High octane number biofuels (methanol, Ethanol, biomethane, biohydrogen) are used in spark-ignition automotive vehicles for applications of two and three-wheelers and passenger cars. High cetane number biofuels (Biodiesel, DME, F-T Diesel) are used in compression ignition vehicles for mainly buses and trucks. Biohydrogen could also be used in proton exchange membrane (PEM) fuel cells. The thermal efficiency of automotive engines fueled with biofuels is higher due to increased combustion efficiency. The octane number, which is higher with biofuels than that of base gasoline, would be helpful to increase the compression ratio of the engines and hence, higher thermal efficiency. The oxygen embedded in hydrocarbon ($\text{C}_x\text{H}_y\text{O}_z$) is mainly responsible for lower smoke/soot / PM as well as CO and HC emissions. The biofuel blends (ethanol-blended gasoline (E5, E10, E15, E85), methanol blended gasoline (M5, M10, M20, M85), biodiesel blended diesel (B5, B20), Hydrogen blended methane (18%HCNG)) is being implemented worldwide in automotive



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Cape Town, South Africa
13-15 December 2021



engines till the complete infrastructure will be developed for the biofuels. Flexible vehicles with multi-fuels compatibility (gasoline and Ethanol, methanol and gasoline, CNG and Hydrogen, etc.) for spark-ignition vehicles and dual fuels (ethanol-diesel, methanol-diesel, biomethane-Diesel, Hydrogen-Diesel, etc.) for compression ignition vehicles working under Reactivity Controlled Compression Ignition (RCCI) mode play a pivotal role for the transition from conventional fuels to green fuels (biofuels). Later, 100% biofuels (M100, E100, B100, H2) could be implemented in automotive vehicles for attaining transport sectors a net zeroemission.

Keywords: Biofuels, Fuel Quality, Internal Combustion Engines, Fuel Cell, Carbon Neutral

fuel

Introduction

The utilization of Biofuels in automotive engines/vehicles is imperative to achieve a part of the sustainable goal of net zero-emission by the year 2050. Biofuel is carbon-neutral fuel as well as a carbon sink. The road transport sector accounts for 17% of global greenhouse gas emissions (UNFCCC). The potential biomass feedstock includes agricultural residue, forest wastes, energy crop products, industrial waste, municipal solid waste, etc., producing biofuels. In addition, Biofuels provides to increase energy security, upgrade fuel quality, reduce regulated and GHGs emissions, increase fuel economy with tangible benefits, including expansion of habitat and food web, improving soil quality, preventing soil erosion, and oxygen generation.

The reserve to production ratio of total proved reserved of oil at the end of the 2020 year is 53.5 [1]. It may be noted that the reserve to production ratio of the oil is very low in Europe (10.4) and the Asia Pacific (16.6). It may be noted that America uses mainly Ethanol as biofuel, which is more than biodiesel, whereas the reverse trend is in Europe and the Asia Pacific. The



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Cape Town, South Africa
13-15 December 2021



consumption of biofuels produced from wastes, residues, and dedicated crops would be projected to about 45% of biofuels consumed in 2030 in the Net Zero Scenario, from 7% in 2020 [2]. Biofuels have a share of 3.3% and have experienced a growth of 13% [3]. Major Infrastructure needs to be developed for higher ethanol blends like E15 and flex fuels like E85.

The possible end of biofuels production with biomass feedstock using different technologies is given in Table 1. Fermentation is more suitable for ethanol fuel with the lignocellulosic biomass feedstock. Anaerobic digestion is for biogas with biodegradable biomass such as animal waste, food waste, etc. Lignin biomass is more suitable for the production of biofuels using the thermochemical process. The biofuels such as Ethanol, biogas, Hydrogen, etc. are produced through biological processes. The biofuels such as methanol, Fisher-Tropsch diesel, Dimethyl Ether, etc. are produced through thermochemical process. The biological process is generally suitable for small and medium-scale biofuel production. The thermochemical method is preferable for large-scale biofuel production.



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Cape Town, South Africa
13-15 December 2021



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TABLE 1: Biomass Feedstock, Technology, and the End product

S. No.	Feedstock	Technology	End product
1.	Energy crops, Forest residue, Crop residue	Gasification, Pyrolysis + Steam Reforming, Partial Oxidation, Autothermal Reforming	Hydrogen
		Anaerobic digestion	Biogas
		Hydrolysis + Fermentation	Ethanol
2.	Oil crops (rape, sunflower, etc.), waste oils, animal fats	Transesterification, hydrogenation	Biodiesel, Renewable Diesel
3.	Sugar and starch crops	Hydrolysis + Fermentation	Ethanol
		Anaerobic Digestion	Biogas
4.	Lignocellulosic biomass	Hydrolysis + Fermentation	Ethanol
5.	Biodegradable MSW, sewage sludge, manure, wet wastes	Hydrolysis + Fermentation,	Ethanol
		Anaerobic Digestion	Biogas
6.	Algae Biomass	Alage residue: Dark Fermentation, Photo-fermentation, Microbial electrolysis, Bio-photolysis	Biohydrogen
		Alage residue: Anaerobic Digestion	Biogas
		Algae oil: Transesterification	Biodiesel

Figure 1 shows the conversion of biomass to biofuels using thermochemical and biological processes. The biomass from agricultural residue, forest residue, energy crop products, municipal solid biowaste, industrial biowaste, etc. can be converted to biodiesel, Dimethyl

Ether, Fisher-Tropsch Diesel, Methanol, Hydrogen, Ethanol, and Biogas. The octane number of biofuels (methanol, Ethanol, biogas, Hydrogen) generally having octane numbers more than 100 can be used in spark-ignition engine vehicles. The cetane number of the biofuels (biodiesel, Fisher-Tropsch Diesel, Dimethyl ether) generally having more than 58 can be used in compression ignition engine vehicles. Hydrogen can also be used in Proton Exchange Membrane Fuel Cell, whereas any biofuel can be used in Solid Oxide Fuel Cell (SOFC).

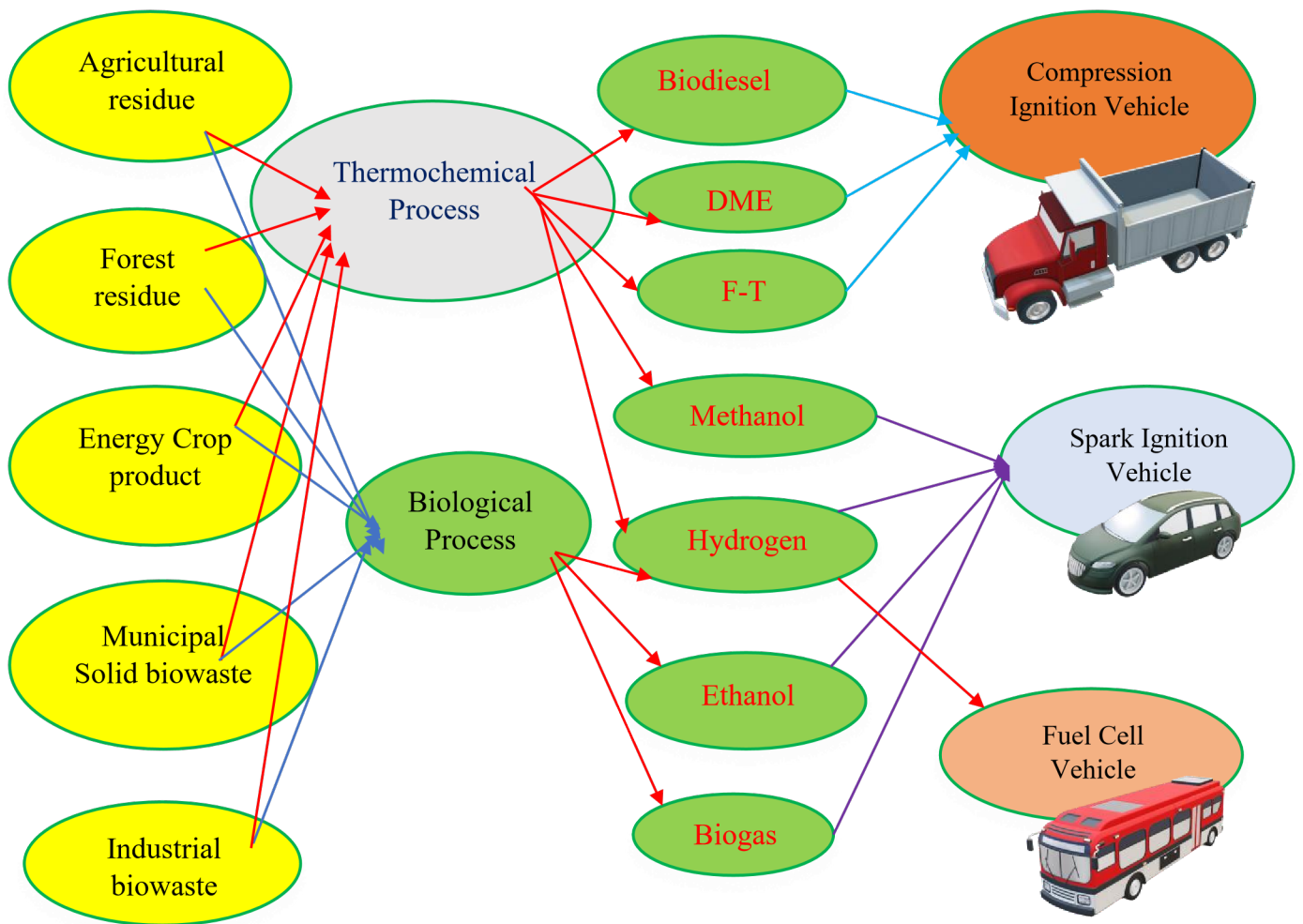


FIGURE 1 - Biomass conversions process, biofuel, and its utilization in automotive vehicles

The world is moving from conventional fuels derived from petroleum oil to alternative fuels, as shown in Figure 2. The conventional fuel gasoline to liquid biofuels such as Ethanol and gaseous fuels such as Hydrogen, dimethyl ether, biomethane, etc..

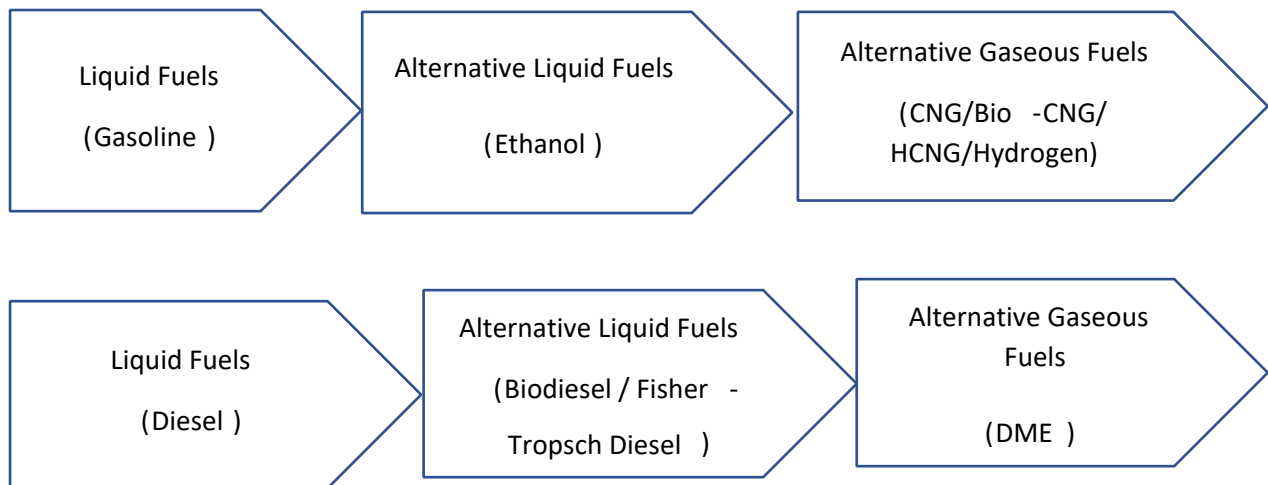


FIGURE 2 - Transition from Liquid Fuels to Gaseous Fuels

Fuel Quality: The important fuel quality includes density, viscosity, distillation characteristics, octane number, cetane number, calorific value, sulfur, copper corrosion number, carbon residue, lubricity, pour point, cloud point, and flashpoint. The viscosity and density of any fuel influence spray characteristics and atomization of the injected fuels. Too high viscosity may result in poor atomization and more energy input to the fuel pump, and lower viscosity results in leakage in the fuel handling system. Hence, the fuel property shall be within the desired ranges. The distillation properties would influence the cold starting, cruise, and high-speed conditions. The fuel must vaporize at low ambient air temperature during starting. All fuel must be vaporized within the available in-cylinder temperature. Otherwise, the not vaporized fuel may lead to poor mixing and emissions and deposits on the inner wall of the engine components [4-5].

The octane number indicates the anti-knocking property. The octane number of some biofuels is given in Table 3. If the octane number is lower than 85, combustion will occur with knock



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Cape Town, South Africa
13-15 December 2021



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resulting in damaging of the engine components and hence, lower engine life. Octane number also provides operating a spark-ignition engine with a higher compression ratio and higher thermal efficiency and thus reduced CO₂ emission. In general, the octane number and cetane number of biofuels have higher than that of petro-diesel or petro-gasoline.

Cetane number indicates the ignition quality of fuels. The cetane number of some biofuels is given in Table 4. A high number indicates better ignition quality as it would get ignition at relatively lower temperatures and improved cold-startability, better transient characteristics, and enhanced engine life. The modern compression ignition engine needs a cetane number of more than 51.

The calorific value of any fuel is essential for better power and torque of the engine. In general, all biofuels except Fisher-Tropsch Diesel have lower calorific value.

Sulfur is generally less in biofuels. Latent heat of vaporization of methanol and Ethanol is higher than that of base gasoline resulting in cold startability problem. To avoid the startability problem, 15% gasoline in ethanol blend (E85) is preferable. Glow plug or other means may be employed to address these technical issues.

High octane number biofuels (methanol, Ethanol, biomethane, biohydrogen) are used in sparkignition automotive vehicles for applications of two and three-wheelers and passenger cars. High cetane number biofuels (Biodiesel, DME, F-T Diesel) are used in compression ignition vehicles for mainly buses and trucks. Biohydrogen could also be used in proton exchange membrane (PEM) fuel cells. Liquid fuels are preferable from a storage point of view, whereas gaseous fuels are preferable from combustion [4].



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Cape Town, South Africa
13-15 December 2021



TABLE 2: Octane Number and Carbon Number of Alternative Fuels for Spark Ignition

Engines / Vehicles		
Fuels	Octane Number	Carbon No.
Gasoline (conventional fuels)	≈ 89-91	C8-16
Gasoline-Ethanol Blend	≈ 95	C2-16
Ethanol	≈ 100	C2
Methanol	≈ 100	C1
Compressed Natural Gas	≈ 110	C1
Hydrogen Blended Natural Gas (HCNG)	≈ 110	C1 (less than 1)
Hydrogen	≈ >120	C ₀

High Octane Number Fuels can be used in Spark Ignition Engines. A high octane number indicates the possibility of higher fuel economy and lower CO₂ emission.

TABLE 3 : Cetane Number of Alternative Fuels for Compression Ignition Engines

Fuels	Cetane No	Carbon No.
Diesel (conventional Fuels)	≈ 51	C16
Diesel-Biodiesel Blend (C16H34)	≈ 51-55	
Fisher-Tropsch Diesel	≈ 75	
Biodiesel	≈ 58	
Dimethyl Ether (C ₂ H ₆ O)	≈ 58	C2



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Cape Town, South Africa
13-15 December 2021



High cetane number fuels can be used in compression ignition engines. High cetane means high ignition quality and better transient engine operation [5].

Application of Biofuels in Automotive Vehicles:

The thermal efficiency of automotive engines fueled with biofuels is higher due to increased combustion efficiency. The octane number, which is higher with biofuels than that of base gasoline, would be helpful to increase the compression ratio of the engines and hence, higher thermal efficiency. The oxygen embedded in hydrocarbon ($C_xH_yO_z$) is mainly responsible for lower smoke/soot / PM and CO and HC emissions.

The biofuel blends (ethanol-blended gasoline (E5, E10, E15, E85), methanol blended gasoline (M5, M10, M20, M85), biodiesel blended diesel (B5, B20), Hydrogen blended methane (18%HCNG)) is being implemented worldwide in automotive engines till the complete infrastructure will be developed for the biofuels. Flexible vehicles with multi-fuels compatibility (gasoline and Ethanol, methanol and gasoline, CNG and Hydrogen, etc.) for spark-ignition vehicles and dual fuels (ethanol-diesel, methanol-diesel, biomethane-Diesel, Hydrogen-Diesel, etc.) for compression ignition vehicles working under Reactivity Controlled Compression Ignition (RCCI) mode play a pivotal role for the transition from conventional fuels to green fuels (biofuels). Later, 100% biofuels (M100, E100, B100, H₂) could be implemented in automotive vehicles for attaining transport sectors a net zero-emission.

Biomass conversions process, biofuel, and its utilization in automotive vehicles

1. Battery Electric Vehicle (BEV):

The electricity generated using renewable energy systems (solar photovoltaic, solar thermal, wind, etc.) is used for Battery Electric vehicles. When the solar radiation falls on silica cells/perovskite cells, it converts into electricity. It further upgrades to desired voltage using power converters (DC to DC / AC) for further electricity transmission and distribution and then reaches the battery charging station/system. A BEV could get charged from the charging system. A BEV is comprised of mainly battery, electric motor, and controllers. The battery shall have high power density and quick charging ability and deliver the desired power with respect to vehicle power and torque demand required from time to time while driving on the



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Cape Town, South Africa
13-15 December 2021



road. Lithium-ion batteries are being used in the batteries due to high power density, but lithium iron resources get limited. Alternative to the lithium iron and further improved battery characteristics, new generation batteries are under development. Lithium mining and processing need substantial energy inputs and need to be addressed. The BEV has a good performance in part-load, specifically in city drive conditions. The regenerating brake for declaration of the vehicles is added advantage compared to internal combustion engines vehicles. The important technical challenges of batteries, including cyclic stability of the electrodes, safety, and fast charge, need to be addressed [6].

The challenges of BEV vehicles include the vehicle range, battery charging time, battery power density, alternative to lithium materials, and battery performance at cold ambient conditions.

2. Hydrogen Vehicles

2.1 Hydrogen fueled internal combustion engines:

Hydrogen can be produced using electrolyzer with the electricity from renewable energy systems as well as gasification/steam reforming process with feedstock of biomass and fossil fuels (coal and natural gas) with carbon capture utilization and storage (CCUS). Hydrogen is a carbon-free energy carrier and does not emit any emissions.

Hydrogen is used in spark-ignition engines due to having a higher octane number (>120). Hydrogen can be injected into the engine's intake manifold called manifold injection and mixed with the inducted air during suction stroke. The ignition of the hydrogen-air mixture is initiated by a spark generated using a spark plug at the end of the compression stroke. The chemical energy of Hydrogen is converted to heat energy and converted to mechanical power by pushing the piston down during expansion stroke. The exhaust gas is expelled into the atmosphere during the exhaust stroke.

Hydrogen-fueled combustion engine vehicles run with higher thermal efficiency due to better combustion. Hydrogen has the property of high flame speed that enhances the constant volume combustion and hence high thermal efficiency. The heat release rate and cumulative heat release are higher with Hydrogen than that of base gasoline resulting in the availability of highquality heat, which is then to be converted to mechanical power.



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Cape Town, South Africa
13-15 December 2021



Hydrogen needs very low ignition energy, but it would negatively affect the preignition during suction stroke. When the hydrogen-air mixture contacts with the residual gas or any external ignition sources, it gets a preignition called backfire. The backfire is a preignition phenomenon that leads to stalling the engine, damaging the engine components and hydrogen handling system. The backfire can be eliminated using delayed hydrogen injection, exhaust gas recirculation, water injection, modified intake manifold, and direct injection.

Hydrogen engine emits a high level of oxides of nitrogen (NO_x) due to the nitrogen in inducted air that reacts with oxygen at high temperature during combustion resulting in the formation of NO_x. The NO_x emissions can be controlled using exhaust gas recirculation (EGR), water injection, retarding spark timing, selective catalyst reduction (SCR), or Lean NO_x Trap (LNT). The varying spark time pertaining to the equivalence ratios and exhaust gas circulation could improve a hydrogen-fueled spark-ignition engine's performance and emission reduction [7].

Backfire could be monitored through measurement of lubricating oil temperature and eliminated by retarding the hydrogen injection during suction stroke using an appropriate electronic control system [8]. Backfire is categorized as deflagration as its velocity is about 230 m/s and is characterized using three phases: ignition delay, backfire propagation, and termination [9].

The hydrogen-fueled engine may experience a power drop due to lower volumetric energy content. The power output could be improved using turbocharging or supercharging technology.

2.2 Hydrogen proton exchange membrane fuel cell:

A fuel cell is an electrochemical device that converts hydrogen to electricity. It has very few moving parts resulting in lower maintenance costs. It does not have the Carnot theorem limitation as it operates at low temperatures as the efficiency of the hydrogen fuel cell is higher than that of hydrogen internal combustion engines. The Hydrogen flows over the anode, and electrons are attracted by the anode and flow through the electrical load, the proton transfer from the anode to the cathode through the proton exchange membrane. The proton reacts with the electron and oxygen is converted to water in the cathode.



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Cape Town, South Africa
13-15 December 2021



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Hydrogen fuel faces numerous technical issues catalyst poisoning due to hydrogen fuel quality, CO, and other traces of non-hydrogen gases. The fuel cell needs high purity of Hydrogen (99.999%). The PEM fuel cell needs proper humidification for proper proton exchange through the membrane. The efficiency of the fuel cell is the highest (~ 45 to 55) among other power movers. The efficiency of the fuel cell could further be reduced by reducing the losses such as activation, ohmic, and concentration and the improvement of material characteristics of the anode, cathode, membrane, catalyst, airflow characteristics, hydrogen flow characteristics.

The transient characteristics of the fuel cell need to be improved. The cost and durability of the fuel cell are other major issues. The issues are being solved for the implementation of hydrogen fuel cell vehicles, and hopefully, the fuel cell vehicles will be implemented soon.

3. Ethanol fueled Vehicles:

3.1 Ethanol fueled internal combustion engines

Ethanol is a carbon-neutral fuel and has a higher octane number (~ 100) than base gasoline (~ 91), and it is known as an octane booster. The embodied oxygen in Ethanol leads to improved combustion and thermal efficiency of internal combustion engines and reduced emissions such as CO and HC. Ethanol can be implemented in a phased manner as it could mix well with gasoline. Depending on the availability of Ethanol, the ethanol-gasoline blends (E15, E85, and E100) can be implemented. Ethanol up to 15% ethanol-blended gasoline does not require any major modification of the engine hardware and fuel handling system. 85% Ethanol blended gasoline (E85) or 100% ethanol (E100) needs a major infrastructure modification. Ethanol in gasoline boosts octane number (RON: 100) and leads to reducing the emissions of CO (75%) and HC (66%) drastically [10].

The thermal efficiency of ethanol-gasoline fueled engines could be enhanced using a higher compression ratio with a significant reduction in CO and HC emissions. However, NO_x emissions increased [11].

3.2 Solid oxide Fuel Cell Vehicles

Ethanol can be used in solid oxide fuel cell vehicles. This is known as a high-temperature fuel cell. The overall efficiency of the fuel is very higher. The Ethanol is reformatted to carbon



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Cape Town, South Africa
13-15 December 2021



monoxide and Hydrogen using a reformer. The Ethanol is passed to a reformer which provides the reaction between the Ethanol with steam (steam ethanol reforming) or CO₂ (ethanol dry forming), or oxygen (partial oxidation reforming) or combined of water and oxygen (autothermal ethanol reforming). The Hydrogen produced using the reformer is passed to the anode and gets further reaction to separate electron and proton. The air is passed to the cathode. The SOFC fuel has the problem of startability and transient response. This is another promising technology for the utilization of Ethanol in SOFC with higher efficiency.

4. Biodiesel fueled compression ignition engines:

A diesel engine fuelled with 100% Biodiesel (B100) emits lower CO, HC, and smoke emissions than base diesel. However, NO_x emission is higher [12]. Greenhouse gas emissions (CO₂, CH₄, and N₂O) decreased with an increased compression ratio fueled with biodiesel [13].

Wall impingement is a technical issue with biodiesel fuelled compression ignition engines due to an increase in spray penetration distance, and this problem can be eliminated by optimizing the injector's nozzle configuration [14].

Spray cone angle, penetration, air-entrainment, Sauter Mean Diameter (SMD) are higher with biodiesel-diesel blends. SMD is higher due to higher density, viscosity, and surface tension. Air entrainment increases due to an increase in penetration distance and vaporisation time because of the larger size of SMD [15].

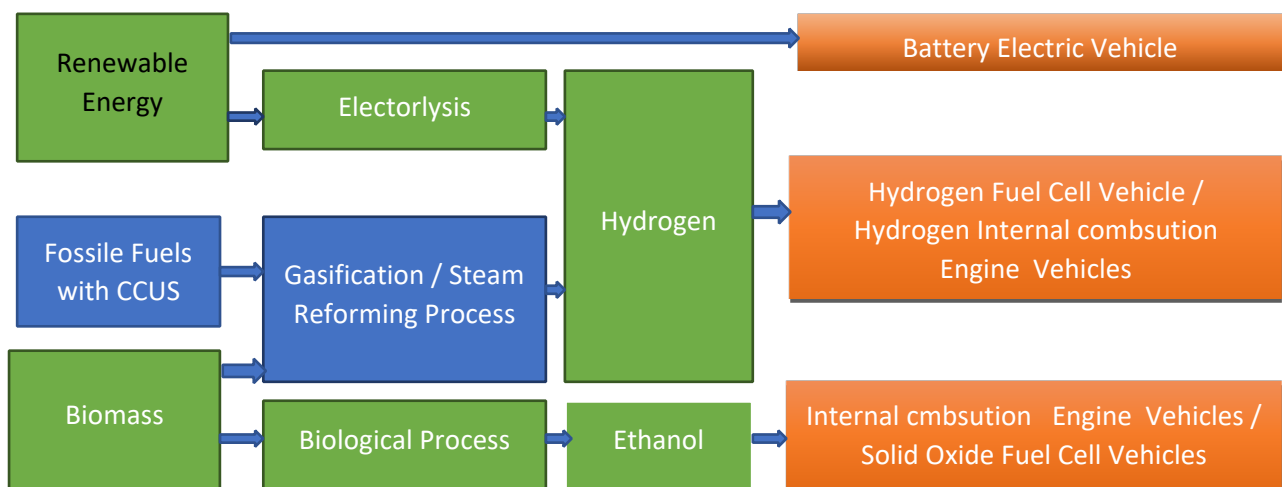


FIGURE 3. A Scenario for Net Zero Emission in Transportation Vehicles



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Cape Town, South Africa
13-15 December 2021



Figure 3 shows a scenario for achieving net zero-emission in Transportation sections by the target year 2050. Electricity, Hydrogen, and Ethanol produced from renewable energy sources and clean energy with CCUS are viable energy/fuels for automotive vehicles. The Battery Electric Vehicles are two and three-wheelers and cars running in urban cities. Hydrogen-fueled engines/fuel cells are vehicles with long-range vehicle travel and heavy-duty passenger and goods vehicles. The ethanol-fueled combustion engine vehicles / SOFC vehicles are the passenger vehicles with long-range.

The transition from conventional fuels to zero-carbon / carbon-neutral fuels is shown in Figure 4. Gasoline, natural gas, and diesel are mainly used as transportation fuels in automotive vehicles. Ethanol is blended in gasoline is one way to move towards a carbon-neutral environment. 15% ethanol-gasoline (E15) could be used in conventional spark ignition engines without major modifications in the engine as well fuel handling infrastructure. A dedicated spark ignition engine needs to be developed for the usage of 100% ethanol. Ethanol could also be used in Solid Oxide Fuel Cell vehicles.

Compressed Natural Gas is mainly used in spark-ignition engines worldwide. 18% Hydrogen blended natural gas (HCNG) is the first step towards Net zero carbon targets in transportation sectors. For the use of 18%, HCNG does not require major modifications in fuel handling infrastructure as well as the engine. For 100% hydrogen, a dedicated spark ignition engine is necessary. Hydrogen can be used in PEM fuel cells.

A diesel-fueled compression ignition engine is generally used for mass transportation (trucks). Biodiesel blended diesel is the first step towards a sustainable transportation sector. 20% biodiesel blended fuel does not need a major hardware modification in the engine. Similarly, Fisher-Tropsch diesel (blended with diesel or 100%), which is similar to diesel properties, could be used in conventional diesel engines. A dedicated diesel engine is necessary for 100% biodiesel and dimethyl ether.

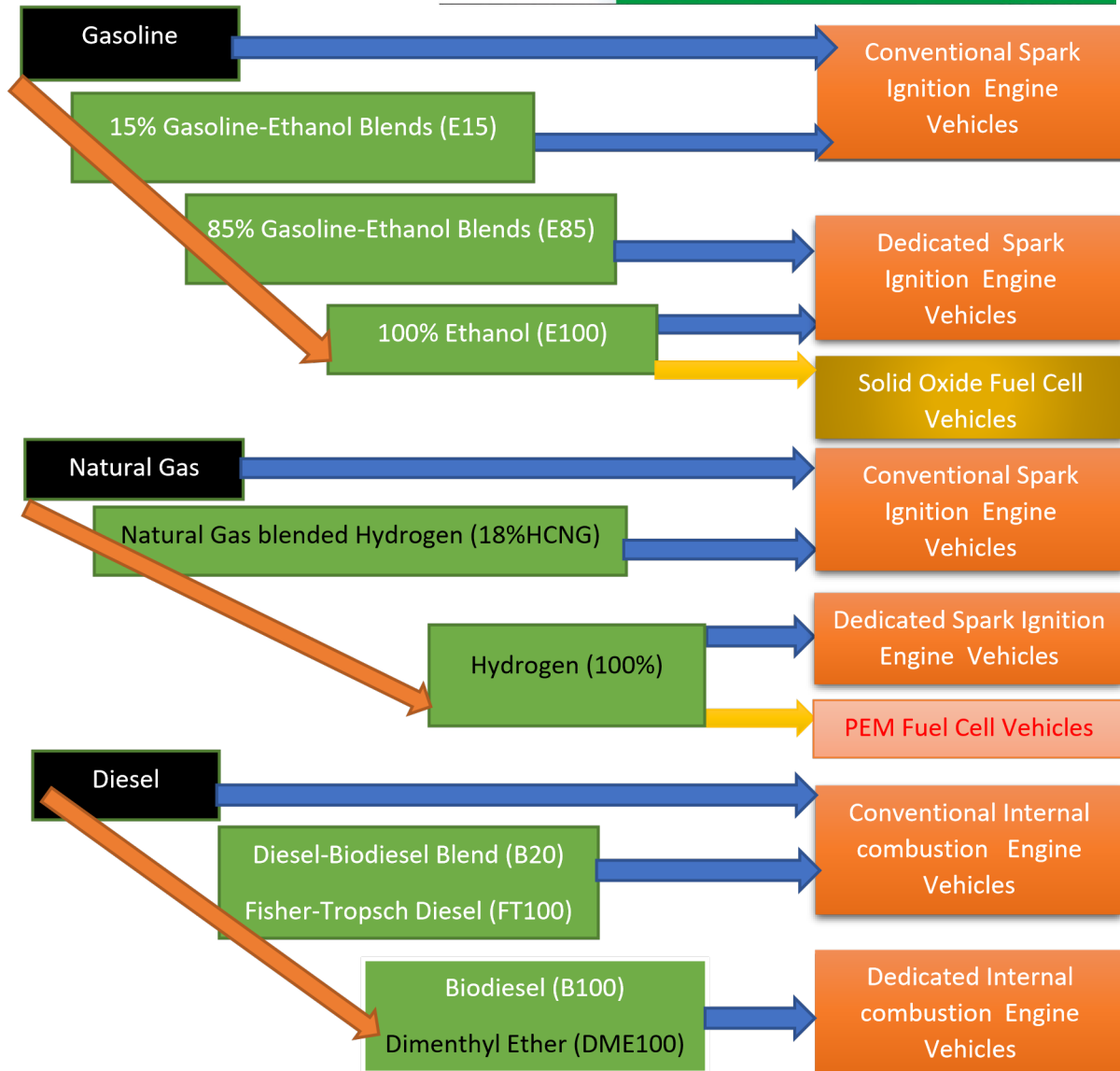


Figure 4: A pathway for Transition from conventional fuels to zero-carbon / carbon-neutral fuels

Conclusions:

- Biofuels could be produced using biomass feedstock from agriculture, forest, industrial, municipal solid waste, sewage sludge, etc.
- Biofuels such as methanol, Ethanol, Hydrogen, biogas, biodiesel, Fisher-Tropsch diesel,



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Cape Town, South Africa
13-15 December 2021



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Dimethyl Ether are preferred for automotive engines.

- Biofuels have higher fuel quality, such as the higher-octane number and cetane number than gasoline and diesel fuels.
- The biofuels could easily blend with Gasoline-ethanol, diesel-biodiesel, hydrogen blended natural, gas, etc. in internal combustion engine vehicles without major hardware modifications and fuel handling infrastructures (value chain). However, dedicated vehicles needst to be developed for 100% use of biofuels for better performance and emissions reduction.
- Biohydrogen could be used in PEM fuel cells for the highest emission with zero-emission
- Any biofuel could be used in Solid Oxide Fuel Cell vehicles with zero-emission except CO₂.
- Ethanol and methanol fuel has a high latent heat of vaporization, leading to cold stability problems.
- All biofuels have lower calorific values that would lead to power drops.
- All carbonaceous emissions such as CO, HC, PM, etc. are lower with biofuels than petroleum fuels.
- DME fueled compression ignition engine could emit near to zero smoke emission as it could lead to sustainability of compression ignition engine
- Biofuels are known as carbon-neutral fuels with a high potential to achieve net-zero emission by 2050.

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Cape Town, South Africa
13-15 December 2021



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