

Design Analysis of a Process Plant for the Production of Bioethanol from Fruit Wastes

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Abstract— This research is centred on analysis of a process plant for the production of bioethanol from fruit wastes. The wastes were first weighed and subjected to treatment (drying, crushing, particle size etc.) then characterized to determine the physiochemical properties with the following results: moisture content (81%), volatile solids (65.92%), total solids (19.23%), ash content (6.56%), fixed carbon (27.52%) and pH (4-10). The elemental composition of the wastes was carried out using the LECO TRUSPEC CHN analyser with results as follows: Carbon (131), Hydrogen (207), Oxygen (93) and Sulphur which gives the chemical formula of the fruit wastes to be $C_{131}H_{207}O_{93}S$. The process plant was simplified into various sections and simulated using Aspen Plus software. The principle of conservation of mass and energy embedded in Aspen Plus software was implemented in the process plant simulation. The mass flowrate of syngas, which is the major component for high yield production rate of bioethanol before and after purification stage, was 667627kg/hr and 686400kg/hr respectively. Ethylene glycol was added during the extractive distillation which resulted in efficient separation of water-bioethanol mixture of 99.83% of pure bioethanol obtained. Results obtained from the ASPEN ENERGY ANALYZER[®]V.11 analysis showed the summary of the flow rates, cost of utilities and carbon emission in the plant. It was observed that a total of 52.38% and 24.96% of the actual total utilities (in flow and cost respectively) could be saved to reduce energy consumption and cost.

Keywords— Fruit Wastes, bioethanol, syngas, biofuel, Aspen plus, Fermentation.

I. INTRODUCTION

In recent years, solid waste treatment has become a serious issue worldwide. Solid waste generation is gradually increasing with the passage of time due to population explosion, urbanization and industrialization. Conventional treatment methods employed for solid waste treatment include land filling, composting, and incineration, etc. However, these techniques have severe ecological impacts and disadvantages associated with them such as air pollution, land pollution, and leachate flow from dumped waste causing water pollution Ramzan *et al.*, (2018). Fruit waste (FW) represent a specific waste produced by markets, homes and by many companies in the food industry. Due to their high perishability, their handling and disposal are quite censorious to community acceptance. Since they contain very high moisture contents, biochemical processes, such as anaerobic digestion, are the most apt conversion technologies to treat FWs. To ensure good conversion efficiencies and process stability, it is imperative to precisely characterize the feedstock properties, especially physical and chemical characteristics like the Total Solid (TS), Volatile Solid (VS), Carbon, Nitrogen, macro, micro and trace elements contents Asquer *et al.*, (2013).

Bioethanol is ethanol produced through processing biological matter, either waste products or crops grown specifically for the purpose of creating ethanol. One of the most promising alternate energy sources is bio-ethanol and it can be produced from a variety of raw materials.

Waste has been a major cause of environmental pollution in the world generally, my case study been the Port Harcourt metropolis especially the market places around Rumokoro, Mile 3, Mile 1 where the major road sides are filled-up with Fruit waste. It has almost been impossible to effectively and successfully manage it even with the presence of RIVWAMA (Rivers State Waste Management Agency) .Thus, the process plant design analysis for the production of ethanol biofuel from fruit waste will not only help to reduce the wastes but also serve as a pilot plant for waste industrial management companies to be established in Port Harcourt and provide employment for the youths thereby reducing unemployment, social crisis in the city and converting waste to wealth.

The aim of this research is to carry out a process design analysis for the production of ethanol biofuel from fruit wastes. Significant scientific attention has been captured due to the production of biofuels from renewable feedstock such as FW. Although some of these feedstock are classified as wastes, they could however be used to supply energy and alternative fuels. Bioethanol is one of the most interesting biofuels due to its positive impact on the ecosystem Arijana *et al.*, (2018).

With the precipitous depletion of the world reserves of petroleum, bioethanol in recent years has spurted as one of the alternative liquid fuel and has instigated immense activities of research in the production of bioethanol and its environmental impact. In light of this, many researchers have sought to determine the best feedstock for the production of bioethanol and to improve on the design and management of waste control schemes. This section of the research centres on the review of past works on the characterization of fruit wastes and design of ethanol plant for production of biofuel.

Nathaniel *et al.*, (2009) studied the identification and characterization of potential feedstock for biogas production in South Africa. They examined the potential substrates that could be used as feedstock for effective operation of an anaerobic digester. They deduced that the use of cassava co-digested with fruit and vegetable waste (FVW) as an alternative feedstock offers a greater

and efficient biogas productivity and could thus be implemented in the biogas projects running with cow dungs inside South Africa, especially in rural communities.

Pratik *et al.*, (2017) carried out production of bioethanol using fruit waste like Indian water chestnut, sweet potato, jackfruit and pineapple. The feedstock was hydrolysed using acid to facilitate their conversion to yield fermentable sugar. A pure culture of *Saccharomyces cerevisiae* was used to carry out the fermentation process and it was seen that different FW had different percentage yield of ethanol.

Oscar *et al.*, (2017) carried out the process simulation of ethanol production from biomass gasification and syngas fermentation. Switchgrass was used as feedstock in the simulation model developed with Aspen Plus of a biorefinery based on a hybrid conversion technology for the production of anhydrous ethanol. Their simulation model presents three modules: gasification, fermentation, and product recovery. Sensitivity analysis was also carried out to study the effects of gasification and fermentation parameters that are key factors for the development of a cost-effective process in terms of energy conservation and ethanol production.

Asquer *et al.*, (2013) carried out detailed characterization study of the chemical and physical properties of representative varieties of fruits and vegetables wastes produced by the Vegetable Wholesale Market of Sardinia in Italy. The study also comments on the practicability of using FVW as a single substrate in anaerobic digestion and estimated the expected biogas composition from the anaerobic digestion of the FVWs.

Ramzan *et al.*, (2010) carried out the characterization of kitchen waste as a feedstock for biogas generation by thermophilic anaerobic digestion. They obtained the proximate and ultimate analysis from the waste collected and generated biogas in a bench scale setup from the waste material for different total solid concentrations. They concluded that their observations support the use of kitchen waste for thermophilic anaerobic digestion and biogas production.

II. MATERIALS AND METHODS

2.1 Materials

The materials and apparatus used to achieve the research objectives include;

- a) ASPEN PLUS[®] version 11.0
- b) ASPEN ENERGY ANALYZER[®] version 11.0
- c) Fruit wastes (orange peels, pawpaw peels and banana peels)
- d) Electronic scale (MODEL: DT 50000 S. METTLER)
- e) Laboratory dry oven (MODEL: DHG-9101-2A SEARCHTECH INSTRUMENTS)
- f) LECO TRUSPEC CHN ANALYSER
- g) Furnace
- h) pH meter
- i) Desiccator
- j) Beaker
- k) Crucibles
- l) Laboratory mortar and pestle

2.2 Methods

The engineering methods adopted for the design are the principle of conservation of mass and energy. Fruit waste characterization, process design, selection and simulation was carried out on ASPEN PLUS software (Syngas production, Syngas purification, Syngas fermentation and Extractive Distillation).

2.2.1 Fruit Wastes Characterization

The preferred FW which includes orange peels, pawpaw peels and banana peels were collected from Mile 3 and Mile 1 markets located in the metropolis of Port Harcourt, Rivers State and stored respectively.

2.2.2 Feed Condition of the FW for Process Simulation

FW which comprises orange peels, pawpaw peels and banana peels was employed for the steady-state process simulation. The FW feed flowing at a rate of 100,000 tonnes/day, temperature of 27⁰C and pressure of 1 atm was considered for the process simulation. Equally, an average particle size of about 2 – 4.5 mm was also assumed for the process simulation. According to Reinhart, (2014), the chemical formula of the FW was formulated to be C₁₃₁H₂₀₇O₉₃S neglecting the ash content and using sulphur as a basis.

2.2.3 Process Description on ASPEN PLUS[®]

The process simulation of the conversion of the FW to biofuel was carried out using ASPEN PLUS[®] V.11.

2.2.3.1 Syngas Production (Gasification)

The syngas production stage consists of five processes which includes drying, crushing, pyrolysis, combustion and steam gasification. To simulate the gasification process, different pre-defined units within ASPEN PLUS[®] were used to simulate several stages to achieve the gasification since ASPEN PLUS[®] does not have a pre-defined unit that could solely be used to simulate the gasification process.

2.2.3.2 Biomass Drying:

In ASPEN PLUS[®], the required FW component does not exist in its database, hence, feed characterization was carried out to help obtain required specification parameters and create the FW feed for the process simulation. Since ash would be formed later in the simulation, two non-conventional components were created to model the FW and ash. In order to characterize the enthalpies of these solids, a pre-specified coal model called HCOALGEN was used. Equally, the densities of these solids were specified using another pre-specified coal model called, DCOALIGT. For both non-conventional solids, PROXANAL, ULTANAL and SULFANAL analysis were entered to specify the physicochemical properties and elemental composition of the solids. Proxanal is the proximate analysis of the component where moisture content, fixed carbon, volatile matter and ash compositions of the FW and ash were specified. This data helps ASPEN PLUS[®] determine the amount of potential volatile and non-volatile matter present in both FW and ash non-conventional solids Fatoni *et al.*, (2014). Ultanal is the ultimate analysis of the FW and contains the composition of the biomass/ash. It shows the percentage of the elemental compositions contained in the FW. Since the non-conventional solid, ash, is basically just completely ash, other compositions are filled in as zero. Sulfanal differentiates between various forms of sulphur present in the non-conventional solids created.

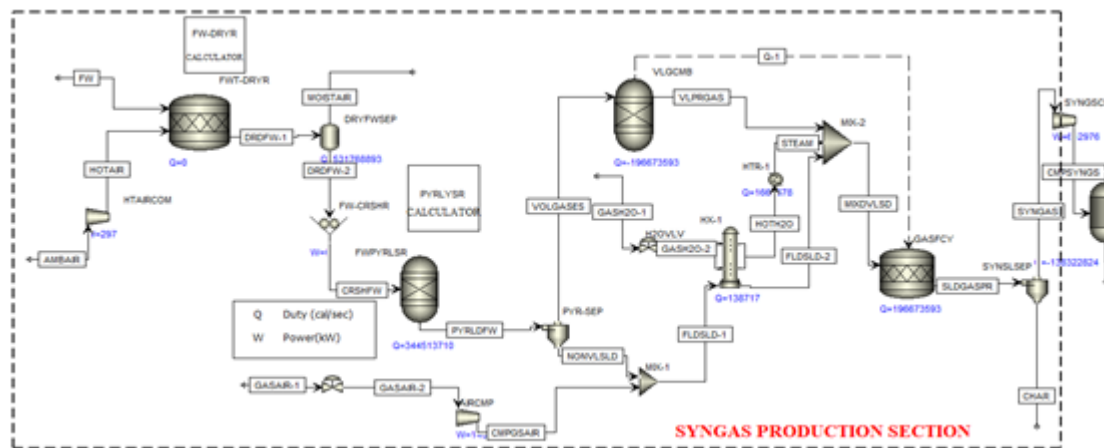


Figure 1: Syngas Production Section from Process Simulation on ASPEN PLUS[®]

To simulate the FW drying, a RSTOIC reactor (FWT-DRYR) was modelled to utilize compressed hot air. Ambient air was compressed using a compressor (HTAIRCOM) and since upon compression the temperature of the air increases, the air stream was then sent into the reactor which reduces the MC of the FW from 81% to 10%. A calculator block (FW-DRYR CALCULATOR) was used to calculate the required MC reduction in the reactor. Variables required for the calculation were created, after which, the executable FOTRAN formula was entered to override previously specified variables within the reactor.

2.2.3.3 Biomass Crushing:

The dried FW from the drying reactor (FWT-DRYR) is further sent to a crusher (FW-CRSHR) where particle size of the FW was reduced from 2 – 4.5 mm to about 950 μm. This is done to make pyrolysis stage itch-free.

2.2.3.4 Biomass Decomposition:

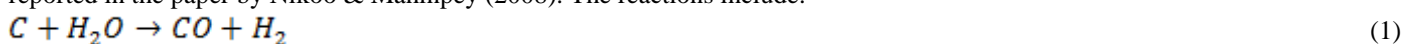
The decomposition of the FW was performed using a RYIELD reactor (FWPYRLSR). In this reactor, the FW was made to decompose into its volatile and non-volatile components. A calculator block (PYRLYSR CALCULATOR), was also used to specify the mass yields of the volatile and non-volatile components. According to Fatoni *et al.*, (2014), the components specified for the volatile product stream were carbon, hydrogen, oxygen, sulphur and nitrogen. On the other hand, solid carbon and ash were present in the non-volatile product stream and this stream was where char formation occurs along with other high carbon source solids. Upon decomposition, the product stream was sent into a separator where the volatile components of 65.92% were specified for the volatile product stream according to the proximate analysis, hence, leaving about 34.08% volatile component in the non-volatile product stream which also contained more of solid carbon and ash.

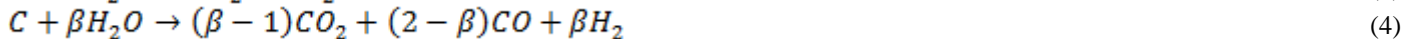
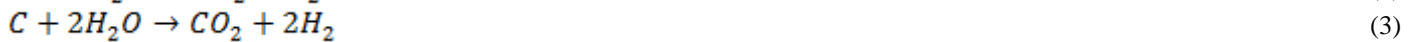
2.2.3.5 Volatile Combustion:

Once the volatiles were separated, they were passed through a RGIBBS reactor (VLGCMB) which ensured volatile combustion assuming that the volatiles reaction followed the Gibbs equilibrium conditions with the reactor operating at 1 atm and 660⁰C Fatoni, *et al.*, (2014). To successfully model this unit, possible products such as CH₄, CO, CO₂, H₂O, SO₂, NO, H₂S and NH₃ were identified.

2.2.3.6 Steam Gasification:

The gasification process was modelled on ASPEN PLUS[®] using a RSTOIC reactor (GASFCY). The product from the volatile combustion reactor (VLGCMB) along with the solid components in the non-volatile product stream were mixed with air and steam and fed into the gasification unit. The process was modelled according to the kinetics, reactions and operating conditions as reported in the paper by Nikoo & Mahinpey (2008). The reactions include:





The value of β can be determined experimentally and ranges between 1.1-1.5 at 750-900°C (Nikoo, *et al.*, 2008). For the model proposed here, the value of β is 1.4. Therefore, Equation 3.9 can be rewritten as follows:



Following the gasification, a cyclone (SYNSLSEP) was added to separate syngas from the unreacted solid carbon and ash mixture. The separation of the unreacted solid carbon and ash mixture may present an opportunity to recycle the left-over solids. However, this can be done only after these particles have been analyzed to present potential to be gasified again. In this case, they are unrecyclable.

2.2.3.7 Syngas Purification

The syngas purification stage consists of three processes which includes CH₄ and NH₃ removal process, H₂S removal process and NO and SO₂ removal process. This stage follows after the syngas production section to purify the syngas for a smoother fermentation process. According to Remco, *et al.*, (2018), to achieve the highest possible conversion, efficiency and productivity for the production of Ethanol, the syngas must be processed. Therefore, a syngas purification section must be designed for removal of the impurities.

a. CH₄ and NH₃ Removal:

The removal of CH₄ and NH₃ was carried out using two reactors; one REQUIL reactor (METAMMPR) and one RSTOIC reactor (METPRFY). The first reactor (METAMMPR) was modelled to remove both CH₄ and NH₃, while the other reactor (METAMMPR), was modelled to remove residual CH₄ composition that managed to get past the first reactor. This was done to ensure the effective removal of CH₄ to avoid contamination of the process in downstream operations.

The process proceeds by compressing the syngas to 10 bars before it is then sent into the two reactors (METAMMPR and METPRFY) for removal of CH₄ and NH₃. The reactions and process conditions as reported in the paper by Remco, *et al.*, (2018), was employed for the process simulation. Both reactors operate at 10 bar and 1500⁰C and the reactions include:



b. H₂S Removal:

The removal of H₂S takes place in a fixed bed reactor (H2SPRFY) at 10 bar and 750⁰C. The bed consists of Zinc titanate (zinc titanium oxide). Zinc titanates are used because they are able to reduce the H₂S concentration to about less than 10 ppm. The TiOx group protects the Zn ions from reduction by H₂ and CO. This allows Zinc titanates to work at higher temperatures than ZnO.

The H₂S removal process operates in two stages. The first stage is the absorption of H₂S using ZnO. This absorption process is known to convert ZnO to ZnS. However, absorption of H₂S stops once there is no more ZnO left. The second stage involves the regeneration of ZnS back to ZnO using O₂. For the regeneration process, the first reactor (H2SPRFY) is closed off from the feed gas, after which, the product from the reactor is sent to a separator (SEP-2), where the gas is separated from ZnS. Furthermore, the ZnS stream is forwarded into a regeneration reactor (REGEN), where O₂ is used to convert ZnS to ZnO and forming SO₂ in the process. The following reactions as reported in the paper by Remco *et al.*, (2018), were specified for the absorption of H₂S and regeneration of ZnS:



c. NO and SO₂ Removal:

The removal of NO and SO₂ takes place in a RYIELD reactor (NOSO2PRY). The operating conditions are 35-50°C and 1 bar Remco *et al.*, (2018). For this process, a solvent which contains KMnO₄ and NaOH is used to dissolve NO and SO₂ in the gas. This is because NO and SO₂ are not soluble in water, hence, the use of the solvent to drive a conversion reaction which could remove them from the gas stream.

According to Remco *et al.*, (2018), dissolving NO and SO₂ is probable by absorption in a KMnO₄ and NaOH solution. NaOH reacts with NO forming NOx ions, while KMnO₄ reacts with SO₂ forming SOx ions. The reactions include:





2.2.3.8 Syngas Fermentation (Biocatalysis Process)

The syngas fermentation process consists of the growth/acidogenesis stage, production/solventogenesis stage, and the condensation/depressurizing stage. For this process, a biocatalyst is needed to aid the fermentation of syngas. Syngas fermenting biocatalysts generally are able to follow the Wood-Ljungdahl Pathway (WLP), also known as the reductive acetyl-CoA pathway as it reduces CO₂ and CO in the presence of H₂. The biocatalysts are known to utilize the pathway to uptake H₂, CO and CO₂ to produce Ethanol, Acetic acid and other byproducts such as Acetone, Lactate, 2,3-butandiol, Butanol and Butyrate Remco *et al.*, (2018).

According to Remco *et al.*, (2018), the fermentation process uses *Clostridium ljungdahlii*, a rod shape, gram-positive anaerobic bacteria, as the biocatalyst (microbe) of choice for the biocatalytic process. *Clostridium ljungdahlii*s selected for this process because it has been known to be one of the very first microbes found to exhibit the aforementioned WLP. It is also known to form primary metabolites, being mostly Ethanol and Acetate from CO, CO₂ and H₂. The microbe is also tailored to favour the production of Ethanol and Acetate as the primary metabolites, hence, the particular strand of the selected microbe will be left unspecified due to the large variety of strands one can choose from, particularly for the said microbe.

To achieve good fermentation and production of primary metabolites, the preferred conditions and reaction kinetics of the microbe need to be understood. Basically, *Clostridium ljungdahlii*s mesophilic, and primarily produces Ethanol and Acetate and its growth and kinetics are strongly affected by pH Remco *et al.*, (2018). A pH of 6 facilitates the growth and acidogenesis process while a lower pH of about 4.5 facilitates solventogenesis, however, discouraging the growth process. Acidogenesis and solventogenesis processes designate the kinetic pathway encouraged at each pH, where acidogenesis describes Acetic acid production, and solventogenesis Ethanol production. Under both acidogenesis and solventogenesis processes, Acetic acid and Ethanol are both produced, but one is produced in excess.

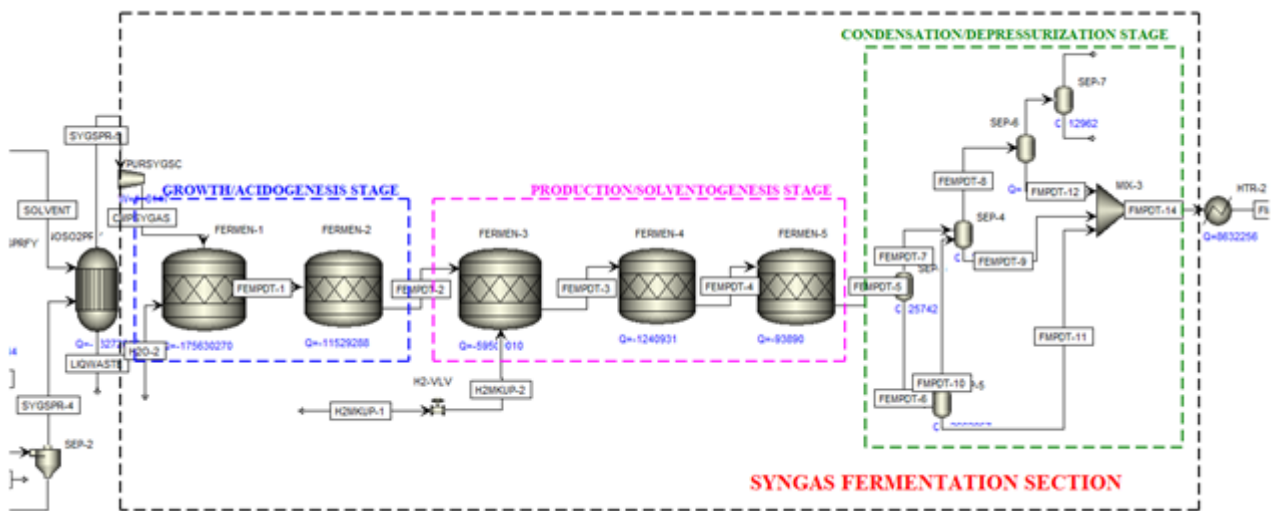


Figure 2: Syngas Fermentation Section from Process Simulation on ASPEN PLUS®

a. Growth/Acidogenesis Stage:

The growth/acidogenesis stage of the fermentation process aims at achieving a product ratio of 13:1 Acetate-to-Ethanol ratio. This stage of fermentation takes place in two RSTOIC reactors (FERMEN-1 and FERMEN-2), with both operating at 35°C and 1 atm Remco *et al.*, (2018). For these reactor models, the reaction equations, fractional conversion and reference component considered were as reported in the paper by Remco *et al.*, (2018).

Table 1: Fractional Conversion Analysis for the Growth/Acidogenesis Stage

Reactions	Reference Component	Fractional Conversion	Flow in Feed (kmol/hr)	Flow Converted (kmol/hr)
$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2$	CO	0.08	18361.2	1468.896
$2CO_2 + 6H_2 \rightarrow CH_3CH_2OH + 3H_2O$	CO ₂	0.08	0	0
$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2$	CO	0.92	18361.2	16892.304
$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O$	CO ₂	0.92	0	0

b. Production/ Solventogenesis Stage:

The production/solventogenesis stage of the fermentation process aims at achieving a product ratio of 20:1 Ethanol-to-Acetate ratio. The fermentation process in this stage takes place in three RSTOIC reactors (FERMEN-3, FERMEN-4 and FERMEN-6), with all the reactors also operating at 35⁰C and 1 atm Remco *et al.*, (2018). The significantly higher product ratio is based on the highest ratio found upon the examination of numerous literatures on production/solventogenesis reactor as reported in the paper by Remco *et al.*, (2018). The reaction equations in this stage are similar to the growth/acidogenesis stage with exception to equation (21) being specified only for FERMEN-3 reactor while other reactors followed the same reactions as that of the growth/acidogenesis stage.

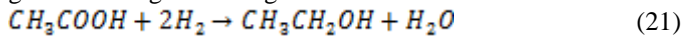


Table 2: Fractional Conversion Analysis for the Production/Solventogenesis Stage

Reactions	Fractional conversion	Reference Component
$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2$	0.95	CO
$2CO_2 + 6H_2 \rightarrow CH_3CH_2OH + 3H_2O$	0.95	CO ₂
$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2$	0.05	CO
$2CO + 4H_2 \rightarrow CH_3COOH + 2H_2O$	0.05	CO ₂
$CH_3COOH + 2H_2 \rightarrow CH_3CH_2OH + H_2O$	1	CH ₃ COOH

d. Condensation/Depressurization Stage:

The condensation/depressurization stage aims at splitting the fermentation product stream into vapour and liquid. This stage comprises of a number of separators (SEP-3, SEP-4, SEP-5, SEP-6 and SEP-7) used for carrying out condensation and depressurization of the fermentation product stream. However, not all the separators operate under the same condition. SEP-3 functions as a split to separate the fermentation product into vapour and liquid fractions and does this under the same operating conditions as the fermentation reactors. SEP-4 operating at 20⁰C and 10 bar simply condenses available Ethanol from the feed streams (FEMPDT-7 and FEMPDT-10) charged into it while SEP-5 operating at 20⁰C and 1 bar condenses and depressurizes the liquid stream (FEMPDT-6). SEP-6 operating at 5⁰C and 10 bar further condenses Ethanol, hence, producing waste gas stream (FMPDT-13) which is further sent to another separator (SEP-7) operating at 5⁰C and 1 bar for depressurization. The aim of this stage is to recover, condense, depressurize and separate Ethanol out from the fermentation product stream which contains mixture of unwanted gases. This stage also facilitates a less strenuous distillation process for purification of Ethanol.

2.2.3.9 Extractive Distillation

The extractive distillation section aims at achieving the production of high purity Ethanol of at least 99%. According to Remco *et al.*, (2018), to achieve this level of purity, conventional fractional distillation is not sufficient, as water and Ethanol form an azeotrope at approximately 95% (wt. %). Numerous procedures exist for achieving this feat on an industrial scale. However, for the purpose of this research project, extractive distillation method was considered.

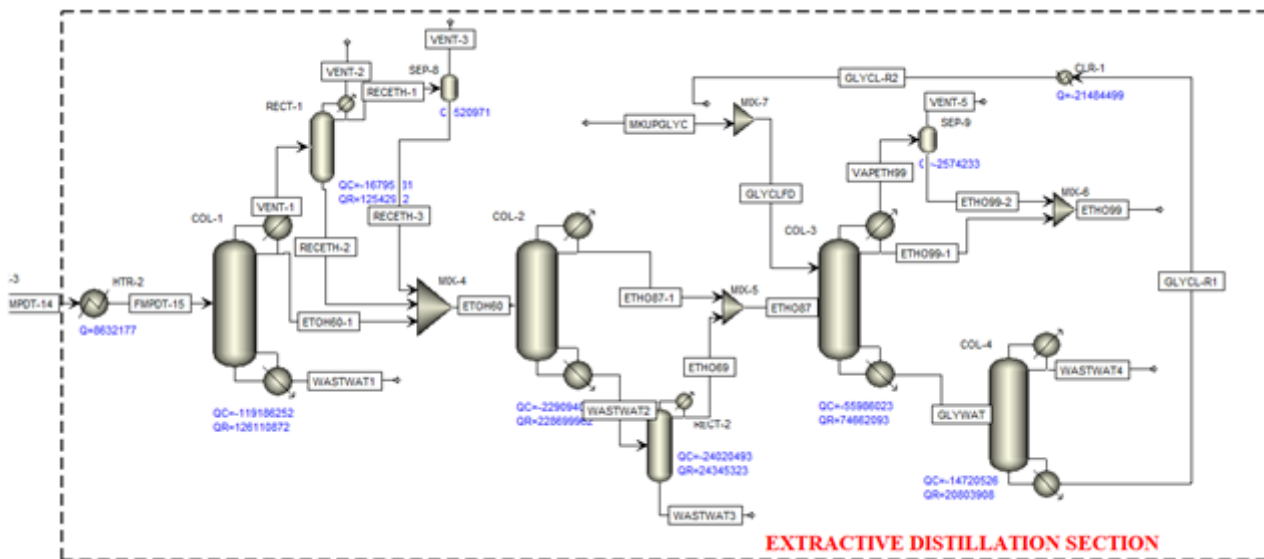


Figure 3: Extractive distillation section from process simulation on ASPEN PLUS®

An extractive distillation process operates by addition of an entrainer in the fractional column. Upon addition of the entrainer, the relative volatilities of the key components are adjusted to favour a more efficient separation Remco *et al.*, (2018). However, for an efficient separation the entrainer needs to possess some vital properties including: Non-volatile and high boiling point, forms no new azeotropes with either components in the mixture and completely miscible with the mixture

a. *Pre-purification Distillation Stage:*

The pre-purification stage consists of three columns (COL-1, RECT-1 and SEP-8). Following the condensation/depressurization stage, all recovered Ethanol liquid streams are mixed and sent to a heater which increases the temperature to about 65⁰C before being sent into the first column (COL-1). A vent was also installed in COL-1 for removal of non-condensable gases contained in the stream. A rectifier (RECT-1) and separator (SEP-8) was also installed to recover condensable Ethanol from the initial vent stream (VENT-1) from COL-1.

b. *Azeotropic Concentration Approach Distillation Stage:*

This stage brings Ethanol concentration to near azeotropic conditions. Concentration of Ethanol was increased to approximately 94% (wt. %) in the column (COL-2), while another rectifier (RECT-2) was also added to recover more Ethanol liquid from the waste stream (WASTWAT2).

c. *Entrainer Injection Stage:*

This stage involves the actual extractive distillation column (COL-3) where the entrainer, Ethylene-glycol, is introduced into the column to drive a more efficient separation and purification of Ethanol. COL-3 is also fitted with a vent (VAPETH99) which contains condensable Ethanol recovered in the separator (SEP-9).

d. *Entrainer Recovery Stage:*

In this stage, the waste stream (GLYWAT) which contains water and Ethylene-glycol is sent to another column (COL-4) to recover the entrainer for reuse. Following the recovery of the entrainer, the Ethylene-glycol stream (GLYCL-R1) is cooled in preparation for recycle.

2.2.3.10 *Energy Analysis*

The energy analysis of the simulated plant was carried out using ASPEN ENERGY ANALYZER[®]V.11. Energy analysis is the traditional method of assessing the way energy is used in an operation involving the physical or chemical processing of materials and the transfer and/or conversion of energy.

III. RESULTS AND DISCUSSION

3.1 *Physicochemical Properties and Elemental Composition of the FW and Ash*

The FW combination sample used as feed for the process design and simulation were characterized and the physicochemical properties and elemental compositions of the FW were determined. As earlier stated, the proximate analysis defines the physicochemical properties such as moisture content, volatile solids, total solids, ash content, fixed carbon and pH value were obtained while the ultimate analysis defines the elemental composition of the FW in terms of their Carbon, Hydrogen, Nitrogen, Oxygen and Sulphur compositions. Tables 3 and 4 show the results obtained from the proximate analysis and ultimate analysis of the FW and specifications for the production of ash as a non-conventional solid respectively.

Table 3: Proximate Analysis (wt. % dry basis) of the FW and Ash

Characteristics (%)	Value (fw)	Value (ash)
Moisture (%)	81	0
Volatile Matter (%)	65.92	0
Ash Content (%)	6.56	100
Fixed Carbon (%)	27.52	0
Total Solids (%)	19.23	0
PH	7.1	Nil

Table 4: Ultimate Analysis (wt. % dry basis) of the FW and Ash

Characteristics (%)	Value (fw)	Value (ash)
Ash Content	6.56	100
Carbon	43.5	0
Hydrogen	5.8	0
Nitrogen	1.98	0
Sulfur	0.87	0
Oxygen	41.29	0

Table 5: Sulphur Analysis (wt. % dry basis) of the FW and Ash

Characteristics	Value (fw)	Value (ash)
Pyritic	0.261	0
Sulfate	0.1305	0
Organic	0.4785	0

The sulphur analysis which tells the breakdown of sulphur composition in the FW sample was also carried out. Table 5 shows the breakdown of the sulphur composition of the FW and ash as non-conventional solids.

3.2 *Particle Size Distribution (PSD) of the FW for Process Simulation*

Particle size distribution of the FW designates a list of values that defines the relative amount, characteristically by mass, of the FW particles present according to size. For the process simulation, FW of PSD 2 – 4.5 mm was assumed and Figures 4 and 5 shows the PSD plot for the FW before and after crushing.

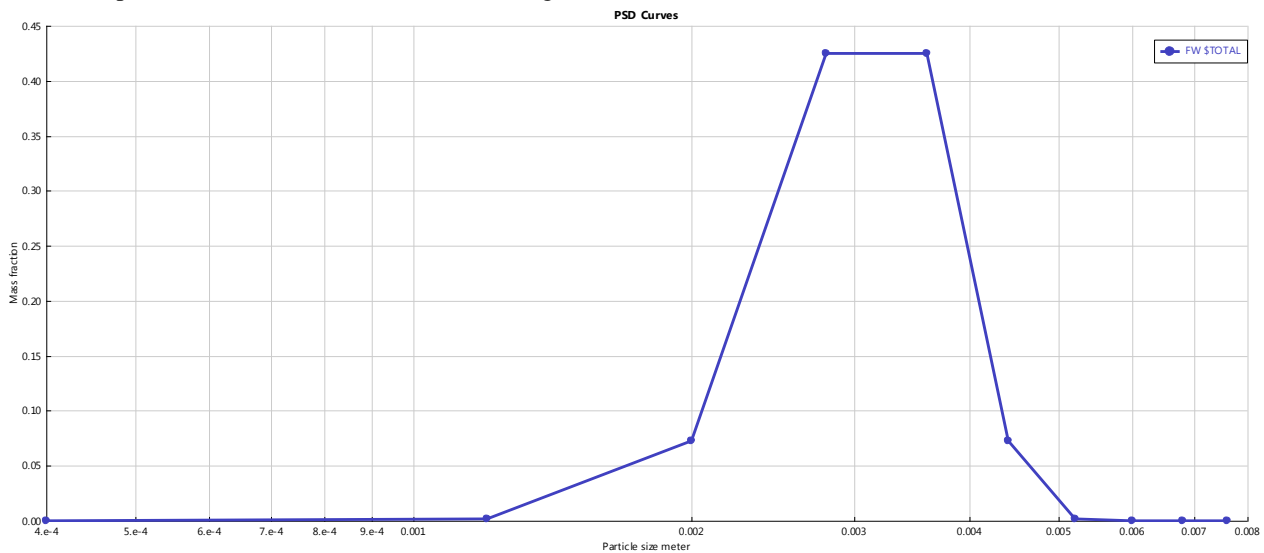


Figure 4: FW (2 – 4.5 mm) Mass Fraction Plot before Crushing

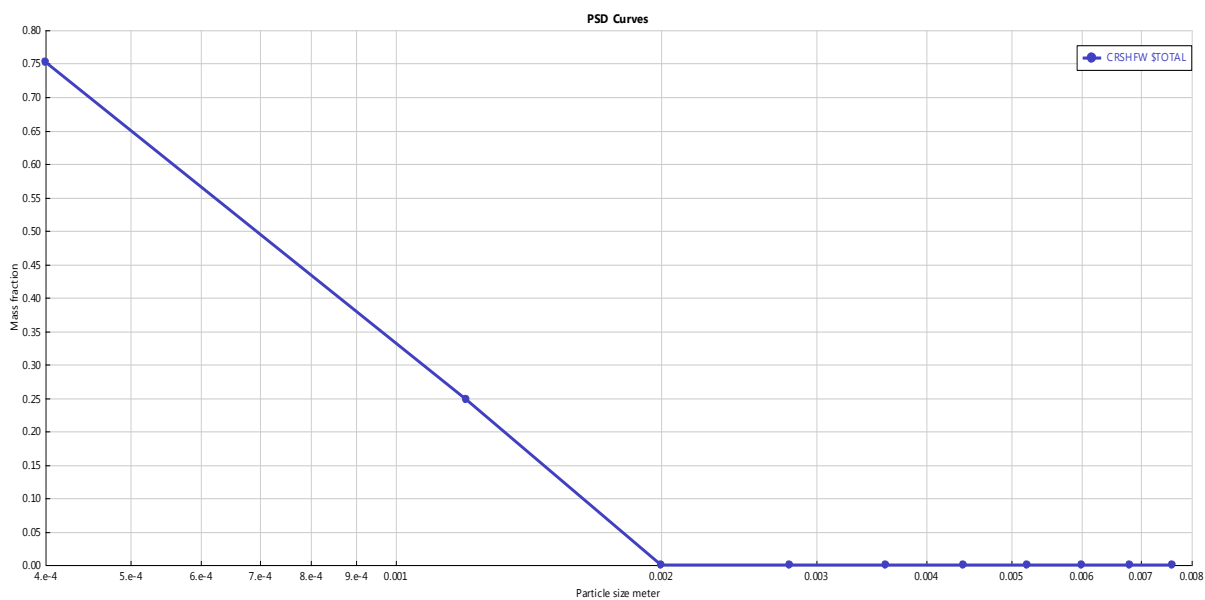


Figure 5: FW Mass Fraction Plot after Crushing

The crusher (FW-CRSHR) was modelled to reduce the particle size of the FW from 2 – 4.5 mm to 950 µm, the result from the FW mass fraction plot after crushing on Figure 4.2 shows that the particle size after reduction ranges between 400 – 1.2 µm. However, more of the particles were dispersed within the 400 µm range which had a mass fraction of 0.75, while the rest spread across the 1.2 µm range with mass fraction of 0.25. This was done to make pyrolysis stage itch free.

3.3 Syngas Production and Purification

Synthetic gas was produced from the processing and gasification of the FW used as feed in the process simulation in ASPEN PLUS®. The production started with the drying and crushing of FW to significantly reduce MC and particle size of the FW respectively. It also involved the pyrolysis, volatile combustion and the gasification process.

Table 6 shows the process conditions and composition of the syngas produced. Following the production of the syngas, it was passed through purification stages for the removal of impurities. According to Remco *et al.*, (2018), this stage is necessary were it prepares the syngas stream for the biocatalytic fermentation process.

Table 6: Condition and Composition of the Syngas

Condition	Value	
Temperature (°C)	1664.8	
Pressure (bar)	1.01325	
Mass Enthalpy (cal/gm)	- 62.3595	
Mass Density (gm/cc)	0.00010619	
Enthalpy Flow (cal/sec)	- 1.15647e+07	
Volumetric Flow (l/min)	1.04785e+08	
Composition	Mass flow (kg/hr)	Mass fraction
Water	652.809	0.000977806
Air	2000	0.00299569
N ₂	4807.84	0.00720138
O ₂	100260	0.150174
CO	344775	0.516419
CO ₂	103986	0.155754
SO ₂	7.96526e-08	1.19307e-11
H ₂ S	4343.1	0.06650528
CH ₄	59326.3	0.0888615
S	2112.53	0.00316424
H ₂	34055.5	0.0510098
NO	2.19263e-09	3.28422e-15
NH ₃	11307.3	0.0169366
Total	667627	1

Table 7: Comparison of Syngas Composition before and after the Purification Process

Composition	Mass Flow before Purification (kg/hr)	Mass Flow after Purification (kg/hr)
Water	652.809	1951.05
Air	2000	1999.99
N ₂	4807.84	14106.4
O ₂	100260	100260
CO	344775	514304
CO ₂	103986	0
SO ₂	7.96526e-08	7.95388e-06
H ₂ S	4343.1	29.9665
CH ₄	59326.3	135.143
S	2112.53	2.7371e-32
H ₂	34055.5	53613.2
NO	2.19263e-09	2.19263e-11
NH ₃	11307.3	1.26862
Total	667627	686400

Table 7 shows the composition of the syngas before and after the purification process for removal of impurities. Syngas is majorly composed of H₂ & CO and seen on Table 7, virtually all impurities were completely removed and the mass flow rate of both components were maximized. Nevertheless, more N₂ and H₂ were added to the stream as a result of the decomposition of NH₃ and conversion of CH₄ in the METAMMPR reactor. Remco *et al.*, (2018) reports that getting rid of the excess hydrogen could be very hazardous. In addition, if H₂ is to be removed using a filter, then it must be neutralized to avert dangers of an explosion.

3.4 Ethanol and Acetate Production

Ethanol and Acetate are both produced in the fermentation section on the process simulation in ASPEN PLUS®. The fermentation stage consists of the growth/acidogenesis stage, production/solventogenesis stage, and the condensation/depressurizing stage. The first two stages used the microbe, *Clostridium ljungdahlii*, following the Wood – LyungaalPathway which uptakes H₂, CO and CO₂ for the biocatalytic fermentation of the syngas, while the last stage facilitates the splitting of the fermentation product stream into vapour and liquid.

Table 8: Acetate and Ethanol Product Rate at the Growth/AcidogenesisStage

Compound	Product Rate (kmol/hr)	Product Ratio
Ethanol	332.636	1
Acetate	8747.16	26.3
Total	9079.796	27.3

The growth/acidogenesis stage aimed at achieving a product ratio of 13:1 Acetate-to-Ethanol ratio, it should be noted that the fractional conversion as seen on Table reflects a selectivity ratio of 11.5:1 Acetate-to-Ethanol, and not 13:1, which is tied to the inherent absorption factor of each of the gases in the process itself as reported by Remco *et al.*, (2018). As shown in Table 8, a product ratio of approximately 26.3:1 Acetate-to-Ethanol ratio is obtained from the process simulation in ASPEN PLUS®.

Table 9: Acetate and Ethanol Product Rate at the Production/Solventogenesis Stage

Compound	Product Rate (kmol/hr)	Product Ratio
Ethanol	9179.92	31825.437
Acetate	0.288446	1
Total	9180.208446	31826.437

The production/solventogenesis stage also aimed at achieving a product ratio of 20:1 Ethanol-to-Acetate ratio. However, there was little to no production of Acetate at the end of this stage. This is as a result of the total consumption and conversion of CO and CO₂ to Ethanol in the FERMEN-4 and FERMEN-5 reactors. Table 9 shows the product rate of Acetate and Ethanol at the production/solventogenesis stage.

Table 10: Process and Composition of the Waste Gas Stream and the Liquid Phase Stream

Condition	Waste Gas Stream	Liquid Phase Stream
Temperature (°C)	5	19.9865
Pressure (bar)	1	1
Mass Enthalpy (cal/gm)	- 14.3838	- 2438.22
Mass Density (gm/cc)	0.000860914	0.80325
Enthalpy Flow (cal/sec)	- 463542	- 5.04837e+08
Volumetric Flow (l/min)	2.24598e+06	15466
Composition	Waste Gas Stream (kg/hr)	Liquid Phase Stream(kg/hr)
Water	55.193	317265
Air	1904.37	95.6221
N ₂	13962	144.443
O ₂	94937.1	5322.79
CO	6.19879	0.0870351
CO ₂	13.3293	9.81411
SO ₂	7.59392e-07	7.19448e-06
H ₂ S	10.6425	19.3239
CH ₄	94.736	40.4065
S	0	0
H ₂	4590.6	1.86698e-06
NO	0	0
NH ₃	0.0482486	1.22037
CH ₃ CH ₂ OH	441.721	422468
CH ₃ COOH	0.000163053	17.3218
Total	116016	745385

The condensation/depressurizing stage was installed in the process simulation in ASPEN PLUS[®] to significantly split the fermentation product stream into vapour and liquid. This stage was necessary as it helps rid the fermentation product stream of some of the non-condensable gases. In addition, it depressurized and condensed the liquid phase out from the fermentation product stream in preparation for the purification and distillation stages. Table 10 shows the process condition and flow rate of various components of the waste gas stream and condensed/depressurized liquid phase stream.

3.5 Ethanol Purification and Distillation

Ethanol purification process as modelled on ASPEN PLUS[®] consists of the pre-purification distillation stage, azeotropic concentration distillation stage, entrainer injection stage and the entrainer recovery stage. This section used extractive distillation method for the purification of Ethanol as water and Ethanol forms an azeotrope at approximately 95% (wt. %). An entrainer (ethylene-glycol) was employed for the extractive distillation process. This was because of its non-volatile nature and high boiling point characteristics; it forms no new azeotrope with the Ethanol-water mixture and it is completely miscible with the mixture.

The pre-purification stage follows after the condensation/depressurization stage which functions as a recovery stage for low pressure liquid Ethanol. The pre-purification stage consists of three units (COL-1, RECT-1 and SEP-8) strategically installed to reduce the flow rate of the mixture to the second distillation stage. In the first column (COL-1), the concentration of water and Acetate of stream (FMPDT-15) was reduced by approximately 68% (wt. %) and 99% (wt. %) respectively thereby facilitating an increase in Ethanol weight and molar fraction from 0.57 to 0.80 and 0.34 to 0.60 respectively.

Table 11: Flow Rate and Mass Fraction of Ethanol in all Product Streams from the Pre-Purification

	Total Stream Flow (Kg/hr)	Ethanol Flow (kg/hr)	Ethanol Mass Fraction
Ethanol Liquid Stream (Etoh60)	530613	422307	0.80
Waste Water Stream (Wastwat1)	209327	145.528	0.000695217
Rectifier Vent (vent-2)	1056.77	43798.2	3.2931e-19
Separator Vent (Vent-3)	4387.75	16.2229	0.00369731

Table 11 shows the flow rate and mass fraction of Ethanol in all product streams from the pre-purification stage.

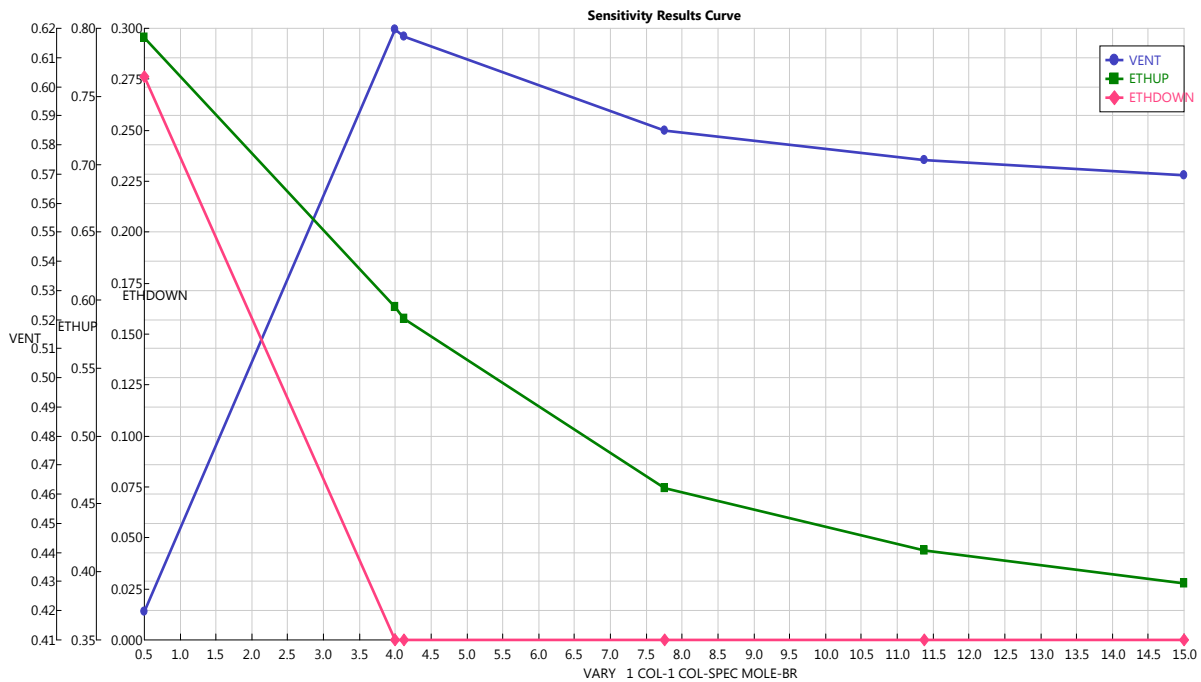


Figure 6: COL-1 Sensitivity Analysis for Optimum Boil-up Ratio

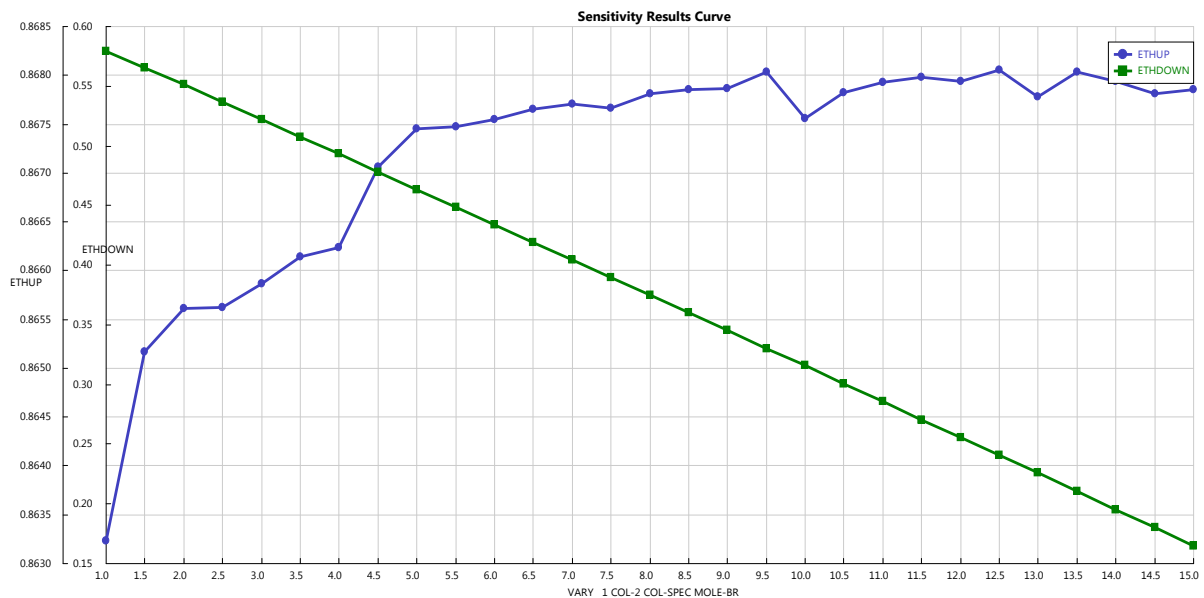


Figure 7: COL-2 Sensitivity Analysis for Optimum Boilup Ratio

The boilup ratio of COL-1 was found from the sensitivity analysis shown in Figure 6, at a ratio fixed of 4, the Ethanol fraction 0.94 in the distillate was high enough for the second distillation stage, while keeping the loss of product in the bottoms as low as possible. However, this selection led to the venting of gases which contained about 0.77 weight fraction of Ethanol at 56,692.2 kg/hr, hence, the need for the RECT-1 and SEP-8 columns to condense and recover enough liquid Ethanol.

The azeotropic concentration approach distillation stage brought Ethanol concentration to near azeotropic conditions. This stage consists of two columns (COL-2 and RECT-2). COL-2 was used for the azeotropic concentration distillation process with the reflux ratio set to 8, while the boilup ratio was kept at 15. This boilup ratio allowed for a high enough Ethanol weight and molar fraction of 0.94 and 0.87 respectively, for the third distillation stage, while keeping the Ethanol fraction in the bottoms low, as can be seen in the sensitivity analysis in Figure 7.

This specification yielded the production of a bottoms rate of 128,753 kg/hr with a recoverable mass fraction of 0.33 Ethanol, the installation of RECT-2 to facilitate more recovery of liquid Ethanol. Table 12 shows the flow rate and mass fraction of Ethanol in all product streams from the azeotropic concentration approach distillation stage.

Table 12: Flow Rate and Mass Fraction of Ethanol in all Product Streams from the Azeotropic Concentration Approach Distillation Stage.

	Total Stream Flow (kg/hr)	Ethanol Flow (kg/hr)	Ethanol Mass Fraction
Ethanol distillate liquid stream (etoh87-1)	401860	379255	0.94
Waste water stream (wastwat2)	128753	43050	0.33
Ethanol distillate liquid stream (etoh69)	48687	41329	0.85
Waste water stream (wastwat3)	80065	1721	0.0215
Mixed ethanol liquid stream (etoh87)	450547	420585	0.93

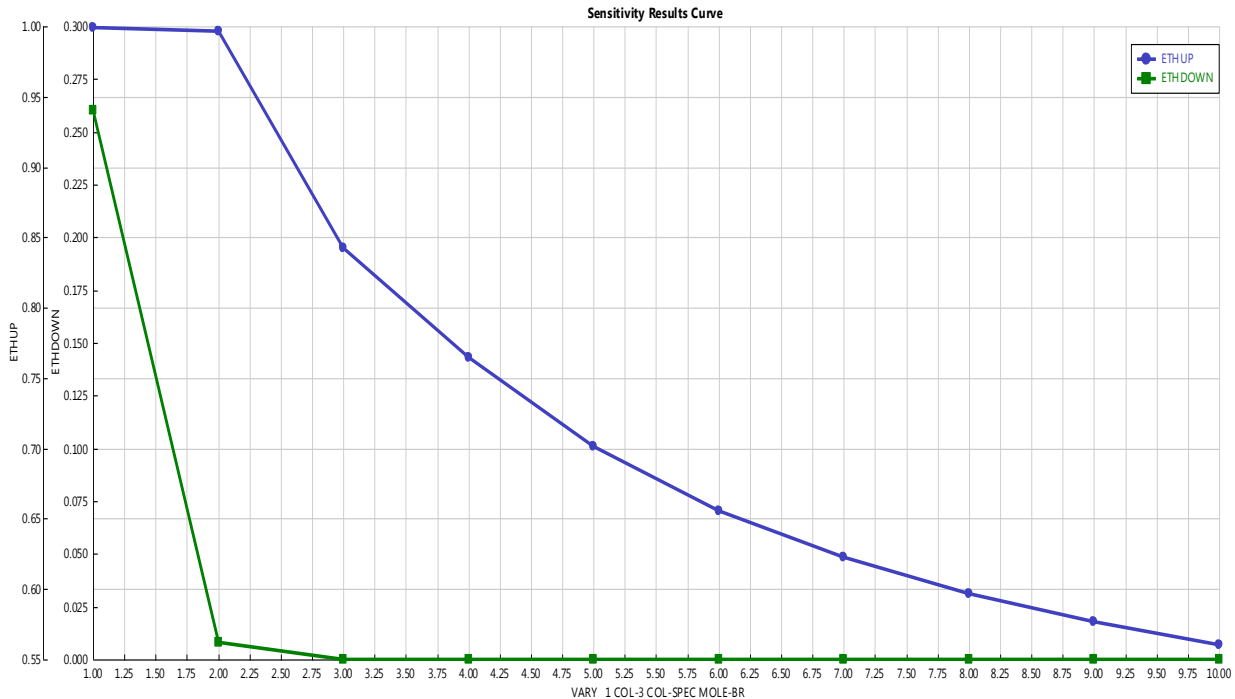


Figure 8: COL-3 Sensitivity Analysis for Optimum Boilup Ratio

The actual extractive distillation process was modelled as the entrainer injection stage in ASPEN PLUS[®]. The process utilized Ethylene-glycol to facilitate an efficient separation of the water-Ethanol mixture. The entrainer was added near the top of the column, to ensure its presence throughout the column. Nonetheless, the entrainer cannot be fed into the column at the very top, because then the Ethanol vapour could carry the solvent to the distillate, which decreases the product purity. COL-3 was used for the extractive distillation process with the boilup ratio set to 2, while the reflux ratio was kept at 1.5. These values were specified according to the sensitivity analysis carried out on COL-3 as shown in Figure 8.

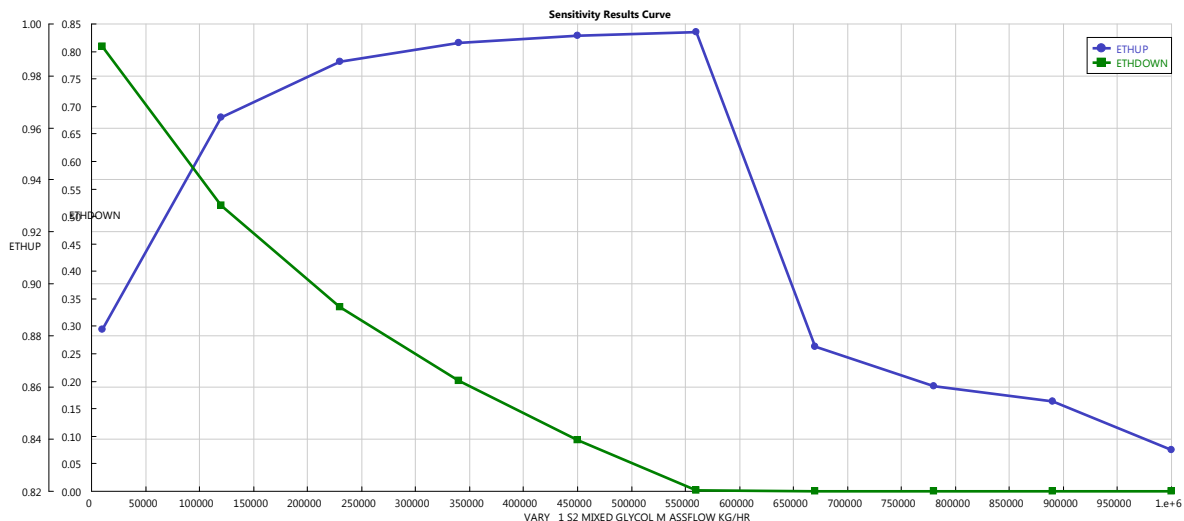


Figure 9: COL-3 Sensitivity Analysis for Optimum Ethylene glycol Feed Rate

The boilup ratio of 2 yielded a very high purity of Ethanol in the distillate, while keeping the product loss in the bottoms rather low. Just as COL-1, in this column 0.1% of the distillate was vented from the reflux drum, to accommodate for the non-condensable gases. An additional parameter was required for an efficient extractive distillation process: the entrainer feed rate. Often, this is defined using the entrainer to feed ratio, or E/F ratio. The aim was to find an E/F ratio that allowed decent separation, but without need for excessive amounts of the entrainer. The optimum E/F ratio was found to be approximately 1.24, with an entrainer flow of 560,000 kg/hr and feed flow of 450,513 kg/hr. The optimal flow rate of the entrainer was found through a sensitivity analysis, shown in Figure 9. As seen in the analysis, the purity of Ethanol product at the distillate increases with the flow of Ethylene-glycol, however increasing the flow rate past 560,000 kg/hr yields a rather lower purity as opposed to the required higher purity.

Table 12: Flow Rate and Mass Fraction of Ethylene-glycol in all Product Streams from the Entrainer Recovery Stage

	Total stream flow (kg/hr)	Ethylene-glycol flow (kg/hr)	Ethylene-glycol mass fraction
Ethylene-glycol in distillate (wastwat4)	32975.55	3.27E-12	9.917E-17
Ethylene-glycol in bottoms (glycl-r1)	560245	559999.994	0.9995

At this boilup rate the Ethylene-glycol recovered is at 99.96% flowing at 560,245 kg/hr. Table 12 shows the flow rate and mass fraction of Ethylene-glycol in all product streams from the entrainer recovery stage.

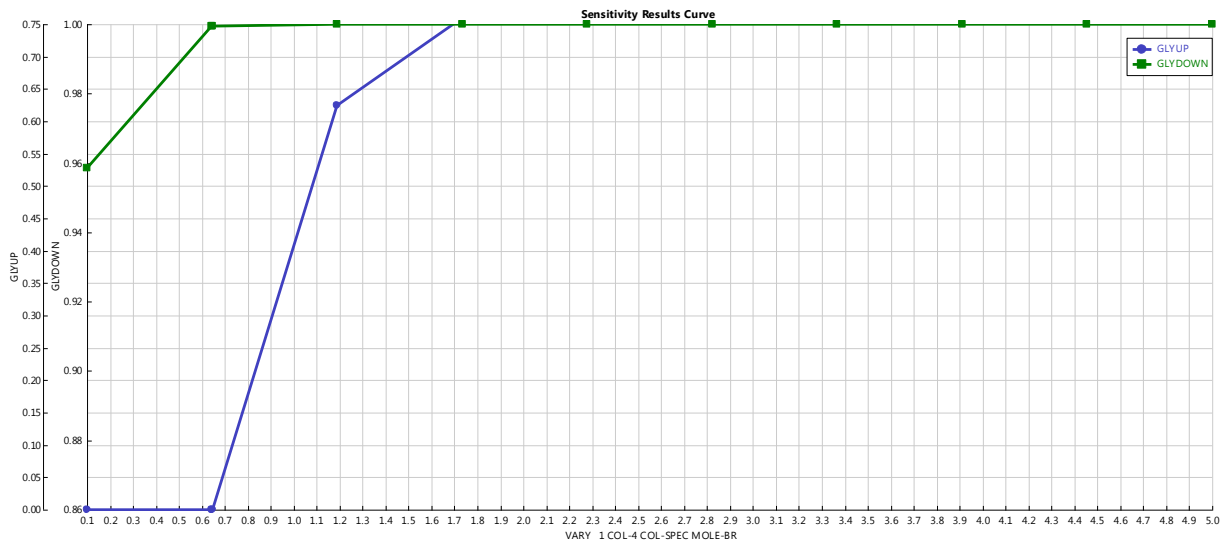


Figure 10: COL-4 Sensitivity Analysis for Optimum Boilup Ratio

The entrainer recovery stage was also modelled to recuperate the used Ethylene-glycol in the entrainer injection stage. Since the bottoms product from COL-3 contained mostly waste water and the entrainer, another column (COL-4), was used for the recovery. The refluxrate and boilup rate for COL-4 were 2.16 and 0.644 respectively. The boilup rate was found through the sensitivity analysis as shown in Figure 10.

Table 13: Columns with their Respective Number of Stages and Optimal Feed Stages from Process Simulation

Column name	Distillation stage type	Number of stages	Optimal feed stage
COL-1	Pre-purification	10	8
RECT-1	Pre-purification	5	2
COL-2	Azeotropic Concentration Approach	20	15
RECT-2	Azeotropic Concentration Approach	5	4
COL-3	Entrainer Injection	25	Ethanol 6 Entrainer 12
COL-4	Entrainer Recovery	15	11

Table 13 shows the various distillation types; pre-purification, azeotropic concentration approach, entrainer injection and entrainer recovery, the number of stages involved in the process stimulation and the optimal feed stage that produces the purest form of ethanol.

3.6 Energy Analysis

A bioethanol plant is generally known to consume energy to achieve syngas production or biomass hydrolysis as the case may be, syngas purification, syngas fermentation, distillation and purification, hence, the need to monitor energy consumption of the process.

Table 14: Flow Summary of the Activated Energy Analysis in the Process Simulation

	Actual (Watt)	Target (Watt)	Available savings (N)	% of actual
Total Utilities (W)	9.296e+09	4.427e+09	4.869e+09	52.38
Heating Utilities (W)	4.314e+09	1.88e+09	2.434e+09	56.44
Cooling Utilities (W)	4.982e+09	2.547e+09	2.435e+09	48.87
Carbon Emissions (kg/sec)	0	0	0	0

Table 15: Cost summary of the Activated Energy Analysis in the Process Simulation

	Actual (\$million/yr)	Target (\$million/yr)	Available savings (\$million/yr)	% of actual (\$million/yr)
Total Utilities	160.4	120.4	40.00	24.96
Heating Utilities	263.3	112.7	150.60	57.20
Cooling Utilities	-102.9	7.698	-110.60	-107.48
Carbon Emissions	0	0	0	0

Tables 14 and 15 show respectively the flow and cost summary of the activated energy analysis results in the process simulation using ASPEN ENERGY ANALYZER®V.11.

IV. CONCLUSION

With the increasing solid waste generation in Port Harcourt metropolis, it is necessary to develop a waste management program capable of handling the incessant waste production problem. Over the years, biorefineries has been employed amongst other technologies and programmes for tackling waste problem by converting waste materials into usable fuel such as Ethanol. Intense researches have been carried out on the conversion of FW to bioethanol. This research aims at converting FW from Port Harcourt metropolis markets into usable biofuel. A typical biorefinery plant was simulated using ASPEN PLUS®V.11. The process simulation was able to yield bioethanol at 99.83% (wt.) with a flow 417,075 kg/hr. For the process simulation, four sections were modelled; the syngas production, syngas purification, syngas fermentation and the extractive distillation section. The syngas production section carried out several functions including drying, crushing, pyrolysis, combustion and steam gasification. This section was able to gasify the biomass (FW feed), after it had been dried for moisture reduction, crushed for particle size reduction and pyrolyzed for decomposition. Following the syngas production section, the purification section was also modelled to remove trace amounts of impurities as their presence could affect other downstream operations. This section was able to significantly reduce H₂S by 99.31% (wt.), CH₄ by 99.77% (wt.), S by approximately 99.99% (wt.), NO by 99% (wt.) and NH₃ by 99.99% (wt.). The distillation and purification section were designed such that four stages were in operation; the pre-purification distillation stage, azeotropic concentration approach distillation stage, entrainer injection stage and the entrainer recovery stage. This section used extractive distillation as water-Ethanol mixture forms an azeotrope at approximately 95% (wt.) purity of Ethanol. Ethylene-glycol was used as the entrainer, sensitivity analysis was also carried out on the columns for better performance and this was able to yield a high purity Ethanol product of 99.83% (wt.) flowing at 417,075 kg/hr. The energy analysis of the plant was also carried out with the use of ASPEN ENERGY ANALYZER®V.11. Results obtained from the analysis shows the summary of the flow and cost of utilities and carbon emission in the plant. It was observed that a total of 52.38% and 24.96% of the actual total utilities (in flow and cost respectively) could be saved to reduce energy consumption and cost. Carbon emission from the plant is of allowable magnitude with almost no trace of emission.

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