

Technoeconomic Analysis of the Synthesis of Ethylene Glycol from Biomass

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Abstract:- The numerous uses of Ethylene Glycol both domestically and industrially has made it become an attractive prospect in the chemical industry; especially in cold climates as antifreeze and in plastic production as well as cosmetics. Thus, there is an economic interest to maximize its productivity and minimize the undesirable excesses that comes with its production. Fossil fuel-based ethylene is the main feedstock of the industrial Ethylene Glycol process which we replaced with Biomass in this project and made it a more environment-friendly production route for this much desired chemical. Sugar Bagasse was used to synthesize Ethylene Glycol after exposing its cellulose structure and further catalyzed in a one-pot reaction by a bimetallic mix of 1 percent Ru-W over activated carbon support, the by-product; propylene glycol was minimized and the utility, mass and energy requirement was determined in the HYSYS simulation environment. Economic analysis revealed that usually the payback period for this project is 2 years on the average ceteris paribus, also the feed basis of 100 kmol/h is relatively more attractive given its marginal cost compared to the opportunity cost of capital, the study also shows that feed rate of over 1000 kilogram-mole per hour is not economically rewarding relative to the marginal change in capital cost and net present value.

Keywords:- Ethylene Glycol; Cellulose; Hysys; Economic Analysis; Biomass, Environment- Friendly.

I. INTRODUCTION

Ethylene Glycol is a very important organic compound used mainly as a raw material in the manufacture of polyester fibers (e.g., PET polyethylene terephthalate), films and antifreeze formulations. It is a toxic, colorless, practically odorless, low-volatility, viscous, hygroscopic liquid. [1] It is completely miscible with water and many organic liquids. Hydroxyl groups on glycols undergo the usual alcohol chemistry, giving a wide variety of possible derivatives. Various pathways to the synthesis of this compound have been in existence, but the techno-economic viability needs to be continually re-analyzed. Over time, Bio-sourced chemicals have become the most environment friendly and economic route to ensure sustainability and applications of green chemistry; this has helped us align a thought process to synthesizing Ethylene Glycol from biomass and to analyze the techno-economic viability of the process(es). Ethylene glycol

is mainly produced industrially from the hydrolysis of ethylene oxide (from ethene)[2].



A. Problem Statement

The prevailing ethylene used to produce EG is derived from non-renewable fossil-based feedstocks, i.e., oil, coal, and natural gas. The starting material or feed, ethylene for industrial production of ethylene glycol is currently steam cracking of crude oil (petroleum). Due to the high pressure of greenhouse gas emission and fossil fuels depletion (reserves are limited), the production of EG variants from renewable resources such as biomass has gained significant attention. Hence, the identification of feasible pathways of Biomass-derived Ethylene Glycol Production is required, then from this list, we intend to comparatively select the most viable technological processes in terms of energy requirements, costs, benefits, risks, uncertainties, and timeframes in order to assess and evaluate economic consequences of new hopeful technology.

B. Scope

This project focuses mainly on the hydrogenolysis process of EG synthesis in order to determine the comparative cost per liter of EG considering the traditional fossil fuel-based route and the biomass-based route(s),

- The study analyzes and compare the technoeconomic performance of the processes with respect to the overall capital cost, the entire production cost, the internal rate of return, and the overall CO₂ emissions.
- to explore the opportunities and challenges of Biomass to EG industry for its efficient, economical and sustainable development

II. LITERATURE

A. The Glycol Compound

According to most sources, French chemist Charles-Adolphe Wurtz (1817–1884) first prepared ethylene glycol in 1856. He first treated "ethylene iodide" (C₂H₄I₂) with silver acetate and then hydrolyzed the resultant "ethylene diacetate" with potassium hydroxide. Wurtz named his new compound "glycol" because of its shared qualities with both ethyl alcohol (with one hydroxyl group) and glycerin (with three hydroxyl groups). In 1859, Wurtz prepared ethylene glycol via the hydration of ethylene oxide. [2] During World War I,

Ethylene Glycol was synthesized from ethylene dichloride in Germany and used as a substitute for glycerol in the explosives industry. Before this, there has not been a record of commercial production of Ethylene Glycol. There is a host of processes that have been developed from different unique organic or inorganic starting materials to produce glycol industrially including the EG synthesis from syngas (a gaseous mixture of carbon monoxide (CO) and hydrogen (H₂) where CO is first converted to dimethyl oxalate (DMO)[3], which is then hydrogenated to form ethylene glycol. Other pathways include the Hydrogenolysis of Cellulosic Biomass (Glucose to EG), Hydrogenolysis of Sorbitol and Xylitol, Transesterification of Bio-Oils (hydrogenolysis of glycerol) and Catalytic conversion of Bio-Ethanol (Ethylene intermediate).[4][5]

B. Biochemical pathways

One of the most widely used polymer, Poly-ethylene terephthalate (PET), was first synthesized in 1941 by Whinfield J.R. and Dickson J.T. during a study of phthalic acid. PET is produced from monomers of ethylene glycol (EG, also named MEG in industry) and purified terephthalic acid (PTA) or dimethyl terephthalate (DMT). [1]

This polymerization process begins with the esterification or transesterification of monomers, and ends with further condensation to produce highly polymerized PET at reaction conditions of 533 K under vacuum of 50 Pa. Commercially, EG and PTA or DMT are produced from ethylene and para-xylene (p-xylene), respectively. Currently in the dominant route for PET synthesis, ethylene is catalytically converted to ethylene oxide over silver catalysts, then the ethylene oxide is hydrated to EG either by noncatalytic or catalytic method.

C. Direct Lignocellulosic biomass conversion to EG

Because of its abundance, estimated at about 2×10^{11} T/year as given by Kobayashi et al (2013), Lignocellulosic biomass has the best potential to be the major feedstock in Biomass processing, consisting of mainly cellulose and hemicellulose (polysaccharides) surrounded by lignin.

Lignocellulosic Biomass requires refining and preparation and that would involve fractionating Lignocellulosic biomass into its three components and render single step treatment procedures such as pyrolysis inefficient in this case, since most of these procedures rely on high temperature, deconstruction which is sensitive in this case is their main focus. Therefore, in order to improve accessibility to the cellulose and hemicellulose, pretreatment options that implies additional processing cost have to be employed. [6]

The lignin content of the Lignocellulosic biomass (which makes up 20-30% of the biomass) acts as both physical and chemical barrier in the extraction of usable sugars and enzymatic conversions process, that is why there is always a section of biomass processing to separate the lignin content to be used in firing or waste in biomass processing. As given by (Parsell et al., 2015) [7], there has been research in converting the waste lignin into even more valuable glucose as inspired by its high carbon content, it

therefore offers even more comparative value to cellulose than its heat content.

Direct conversion of cellulose to Ethylene Glycol has been experimented but yet only with minimal implementation as the industrial feasibility of the process is yet sensitive. The process considers the use of transition metals as catalysts in sensitive combinations and activity (W, Sn, Ni, Cu, Ru/NbOPO₄ catalysts) for selective production of EG. [8]. The yield of EG and observable side reactions is compared using these different catalysts, depending on which products the atom economy proves beneficial.

At the initial stages in hydrothermal conditions, cellulose was hydrolyzed to water-soluble oligosaccharides and glucose at elevated temperatures. The catalytic reactions of tungsten species allow C–C bond cleavage to occur in the water-soluble oligosaccharides and glucose, this yields the intermediate product of glycolaldehyde (GA), via retro-aldol condensation (RAC) while the transition metal subsequently catalyzes the hydrogenation of GA, eventually resulting in the formation of EG.

The homogenous tungsten species (such as tungsten bronze HxWO₃) are very uniquely active for the RAC reaction. Besides the major route for EG production, glucose isomerization happens in a minor route to form fructose, which produces 1,2-PG after a series of reactions involving RAC reaction, dehydration, rearrangement, and hydrogenation [9].

A synergistic effect was observed between tungsten and the other transition metal in a bimetallic combination for the cellulose conversion reaction. For instance, EG was produced with a high yield of 61.7 % over the Ru–W/AC catalyst, as opposed to the small amount of EG that was obtained on either the W/AC or Ru/AC catalysts separately. [10].

It was demonstrated that W⁵⁺-OH species on the surface of WO₃ (solid acid) act as active catalytic sites where the cleavage of the C₂-C₃ bond in glucose, forming glycolaldehyde which is then hydrogenated to EG on the Ru/C surface. [11], [12].

III. METHODOLOGY

In this study, an economic model for Ethylene Glycol (EG) production pathways using biomass (hydrolysis) was employed and compared with the common industrial pathway(s) using fossil fuel to determine the comparative advantages using biomass to using non-biomass starting material.

The cost analysis of the technology (that considers the entire plant requirements for these processes) considers the capital cost and will be a major factor in determine the break-even points for each project.

When considering Cellulosic Biomass processing, outcomes depend on the adopted route, Pyrolysis would yield Bio-oil/fuels, Gasification will generate syngas that can be

processed into several organic compounds, and Hydrolysis will result in convertible sugars or organic chemicals.

A. Biomass Preparation

The preparation depends on the choice of Biomass taken in account, a wide range of lignocellulosic biomass can be used, but for specificity in this project we consider Sugarcane Bagasse for the following reasons.

- There are at least over a dozen Sugarcane producing countries in the world including; Brazil, India, China, Thailand, Mexico, Colombia, Philippines, United States as major producers with Nigeria being the 50th in the world with 1.5 million metric tonnes per year.
- They are available as waste at no extra cost to the currently operating sugar refineries.
- Over 540 million metric tons per year of sugarcane bagasse are produced globally [13]
- Good cellulosic content, and low lignin. The Cellulose content is usually up to 35%, hemicellulose around 30% and Lignin up to 24% the rest mostly comes out as Ash on analyses.

B. Treatment and Reaction

As suggested by experimental yield (Pang et al., 2018) [14], this project adopted mild ball milling to unlock the cell structure followed by Alkali pretreatment method using 10% Sodium hydroxide solution, which comes after the bagasse has been milled and dried.

According to Li et al., 2018b; Detailed structural studies showed the crucial importance of surface Lewis Acid Sites (LAS) formed upon adsorption of water on the surface of WO₃ for cellulose conversion to EG. The catalyst based on hexagonal nanorods h-WO₃ crystals and containing the largest number of LAS allows for the highest EG yield (up to 77.5%)

After pretreatment stage; the substrate is then heated and hydrolyzed (hydrogen gas is dosed at 4 MPa) in the Ru-WO₃/AC fixed bed reactor at 240°C. The ethylene glycol is obtained finally after distillation.

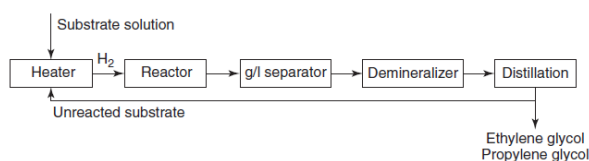


Fig 1:- Flow diagram for the cellulose conversion process

C. Aspen Hysys Simulation

The flow modelling simulator is employed for full scale estimation of equipment sizing, energy balance, mass balance, utility sizing and the project economics.

From the flowsheet the unit operations involve the following steps.

- The raw biomass (sugarcane bagasse 35% cellulose, 30% lignin, 25% hemicellulose) is crushed in a crusher (or ball miller) at room temp and atmospheric pressure.

- To expose the cellulose content of the biomass we wash with 10% NaOH solution, the mixture is decanted to remove mostly lignin and impurities.
- The decanted substrate becomes the feed to the BATCH reactor (which is essentially cellulose).
- Assumed FEED RATE is 50,000 tonnes/year, that is approx. 5000 kg/hr.
- A heater is required to raise feed temperature to 240°C and Hydrogen is dosed at 4MPa into the reactor.
- it is an actual One Pot reaction where about 3 major reactions need to take place to produce EG.
- The reaction is catalyzed by a bi-metallic tungsten oxide-ruthenium over activated carbon catalyst to ensure 100% conversion and up to 70% selectivity (yield) to EG.

The involved reactions as modelled are:

- Cellulose (C₆H₁₀O₅)_n + nH₂O → Glucose nC₆H₁₂O₆ 100% conversion by hydrolysis (+ Fructose on isomerization of glucose)

Glucose may isomerize to Fructose too here but it is not the main reaction desired since it will lead to PG instead of EG.

- Glucose C₆H₁₂O₆ → Glycolaldehyde 3C₂H₄O₂ by RAC retro-aldol condensation (side reactions yields erythrose by RAC and sorbitol by catalytic hydrogenation, erythrose readily hydrogenates to EG).

Also, for the fructose in reaction 1, Fructose C₆H₁₂O₆ → Glyceraldehyde C₃H₆O₃ by RAC (side reactions yields 1,3-Dihydroxyacetone RAC and mannitol by catalytic hydrogenation).

- Glycolaldehyde C₂H₄O₂ + H₂ → Ethylene Glycol EG C₂H₆O₂

Glyceraldehyde 2C₃H₆O₃ + 2H₂ → Propylene Glycol PG 2C₃H₈O₂ + O₂ by hydrodeoxygenation.

In reality, a One pot reaction is the way to represent this reaction but as indicated above, the reaction is simulated in three reactors since isomerization (equilibrium) reaction cannot be modelled in the same pot as conversion reactions and ranked successfully.

- The Ethylene Glycol comes out of the reactor with other products like some Propylene Glycol and Polyols (mannitol, sorbitol) which is then sent to the fractionator to separate the mixture.
- Some of the unreacted substrates may be sent back to the reactor.
- The EG is sent to storage.

IV. RESULTS

This project focuses on the use of a simple systematic and analytic model using overall associated cost data to evaluate the economic feasibilities of the known and considered process routes. Since they all use biomass as a feedstock, the process routes listed are very important in solving the major problem of CO₂ emissions and align with the goals of sustainable development. The CO₂ emissions can be compensated by the CO₂ captured by the vegetables or plants. This drastically reduces the CO₂ emissions; then along

the life cycle of such chemicals or plastics in some cases, there is more CO₂ consumed than produced, meaning a negative

mass balance. The goal of this approach is to help develop a process that is both sustainable and highly efficient.

A. Mass Balance From Streams Composition

Input Stream	MASS FLOW kg/h	Output Stream	MASS FLOW kg/h
CRUSHED BIOMASS	8107.12	Pretreatment vent	0.0000
NAOH	10.0000	reactor vent	29.3705
HYDROGEN	302.382	PG	2975.05993
WATER	1801.528	EG	7205.88967
		H2 & STEAM'	10.715071
Total inflow	10221.0300	Total outflow	10221.0300

Table 1:- Mass Balance analysis.

$$\text{Overall Yield, EG YIELD} = \frac{\text{mass or moles of EG produced}}{\text{mass or moles of reactants converted}}$$

$$= \frac{7206}{8107+302.4+1802} = 0.7057$$

Thus, EG yield is 0.7057 i.e., 70.57% in this simulation case.

B. Energy Balance

Input Stream	ENERGY FLOW Btu/hr	Output Stream	ENERGY FLOW Btu/hr
CRUSHED BIOMASS	-51856560.95	pretreatment vent	0.000
NAOH	-131077.983	reactor vent	5835.414
Q-100	243205.287	COND 2	60674558.827
Q-102	37273.482	PG	-16312086.02
Q-101	2832121.337	EG	-55786896.09
HYDROGEN	20466.636	H2 & STEAM'	-101184.551
WATER	-26536796.21		
REB 2	61064849.589		
Q-103	2798224.484		
Total inflow	-11528294.3	Total outflow	-11528294.3

Table 2:- Mass Balance analysis

C. Executive Summary

Simulator Type: Aspen HYSYS

PROJECT NAME: ETHYLENE GLYCOL SYNTHESIS FROM BIOMASS

CAPACITY: 139256676 LB/Year

Price of EG @ 0.635 USD/LB

PLANT LOCATION: Nigeria

SCHEDULE:

Start Date for Engineering 1-Nov-21

Duration of EPC Phase: 21Weeks

Length of Start-up Period: 52 Weeks

INVESTMENT:

Currency Conversion Rate: 1 USD/U.S. DOLLAR

Total Project Capital Cost: 9.76E+06 USD

Total Operating Cost: 2.52E+07 USD/Year

Total Raw Materials Cost: 2.11E+07 USD/Year

Total Utilities Cost: 690305 USD/Year

Total Product Sales: 1.04E+08 USD/Year

Desired Rate of Return: 20%/Year

Payback Period: 2.14178Years

PROJECT COSTS

CAPITAL COSTS PARAMETERS

Working Capital 5%

GENERAL INVESTMENT PARAMETERS

Tax Rate: 40%

Interest Rate: 20%

Economic Life of Project: 20 years

Salvage Value (Fraction of Initial Capital Cost): 20%

Depreciation Method: Straight Line

ESCALATION

Project Capital Escalation 5%

Products Escalation 5%

Raw Material Escalation 3.5%

Operating and Maintenance Labor Escalation 3%

Utilities Escalation 3%

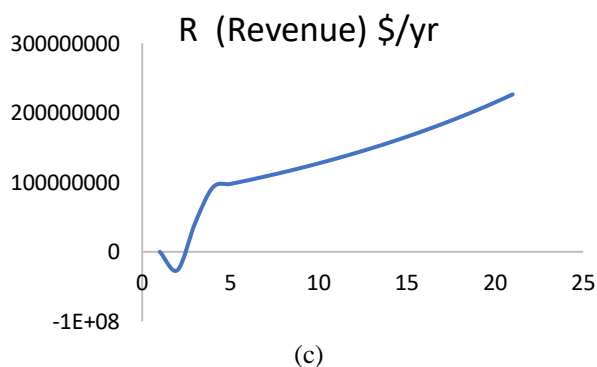
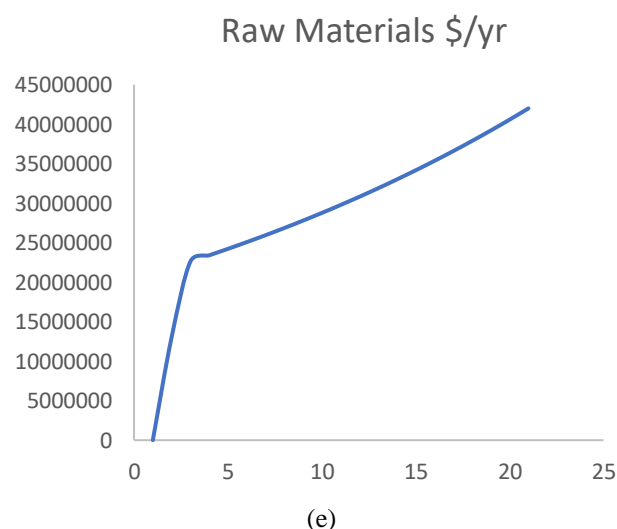
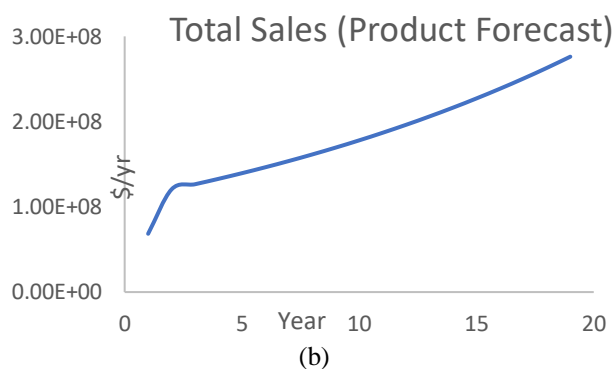
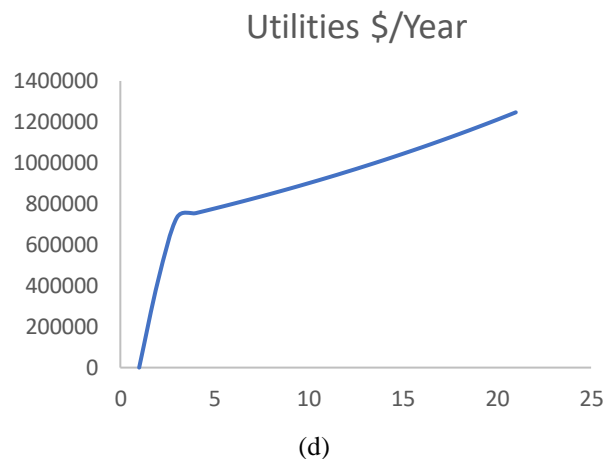
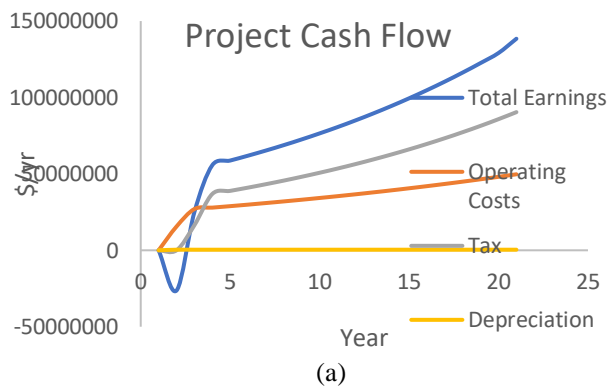


Fig 2:- (a-e). Graphs representing the Project Cash Flow for the Project

D. Sensitivity Analysis

The table below represents the key parameters in the economic analysis for the 20-year life of the Ethylene Glycol plant based on the same equipment list and feedstock variables but with the respective resizing and re-costing data.

BIO-MASS MOLAR FLOW KMOL/H	EG YIELD KG/H	CAPACITY (LB/Year) For EG @ 0.635 USD/LB	PROJECT CAPITAL COST (\$)	PROJECT NET PRESENT VALUE \$	MODIFIED IRR%	PAY OUT YEAR	P-INDEX
1	144	6,161,315	7.44E+06	259953	20.06	18.27	1.01
10	1906	70,603,173	8.46E+06	1.29E+08	24.72	1.78	2.16
50	7206	139,256,676	9.76E+06	2.35E+08	23.35	2.14	1.73
100	16240	689,548,379	11.5E+06	1.36E+09	25.41	1.12	2.41
250	42960	830,294,718	15.1E+06	1.61E+09	25.29	1.16	2.37
500	86910	1,679,650,616	18.5E+06	3.26E+09	25.36	1.12	2.39
750	122700	2,371,667,459	22.1E+06	4.58E+09	25.36	1.11	2.40
900	130400	2,487,144,690	24.7E+06	4.85E+09	25.34	1.12	2.39
1500	216200	4,180,873,781	57.2E+06	7.56E+09	25.27	2.00	2.36

Table 3:- Sensitivity analysis on a 20 years life of plant with varying capacity

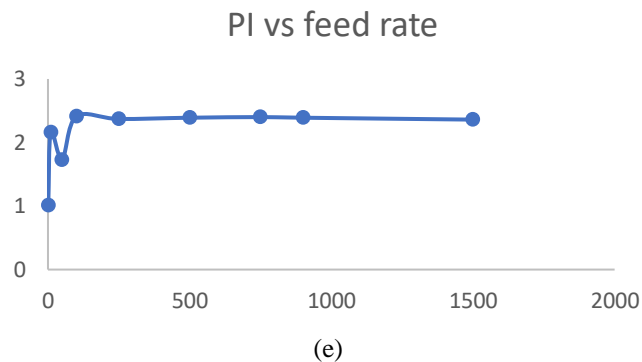
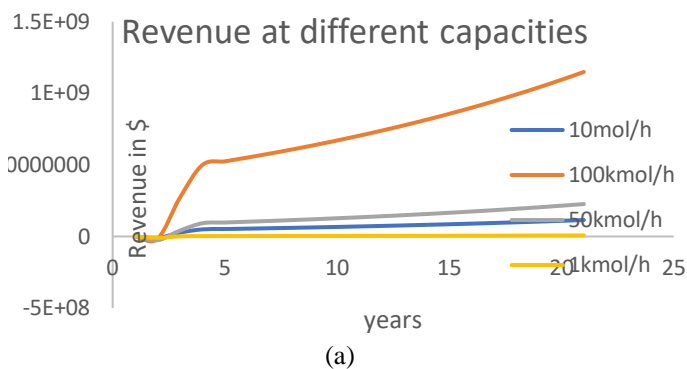


Fig 3:- (a-e) Sensitivity analysis for the Project Cash flow

From this analysis we deduce that the optimum Biomass feed rate basis is 100kmol/h based on this design since the marginal difference in in project cost with respect to the net present value is attractive, also the project becomes non profitable for feed rates lower than 10kmol/h.

Exploiting Higher Production rates yields a higher NPV but becomes unattractive with feed rates exceeding 950 Kmol/h as the marginal increments in NPV may not justify the large changes in capex as shown.

V. CONCLUSION AND RECOMMENDATION

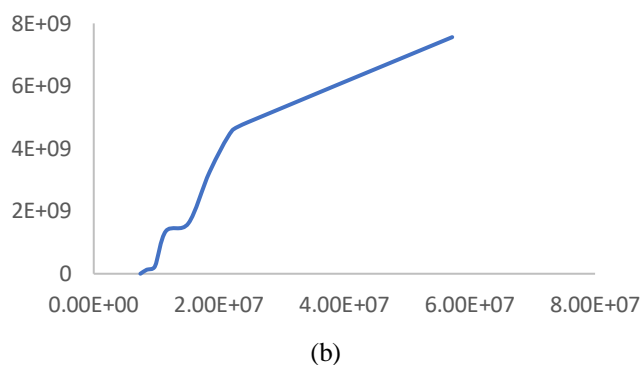
It has been demonstrated in this project by its attractive economics that bio-synthesis of Ethylene Glycol is feasible and profitable both to the environment and prospective investors. The average payback period for this project is 2 years and the use of EG is not going away anytime in the next 3 decades with advancement in technology and other prevalent conditions. In Nigeria the feedstock is available (about 1.5 million tonnes of Sugar Bagasse) and the plant/trains can be tailored to absorb the market or at least improve competition.

The usual point referred to as a setback in the use of Biomass such as Bagasse, Corn stover and other agricultural waste is the effect on the nutrient cycles because these wastes contribute significantly in keeping the soil healthy for planting, evacuation from the cycle may leave future planting practice in serious nutrient deficit, also protection from Land water and wind erosion is a service provide by these wastes on the top soil. We also need to mention the energy input required to extract and process the feed; it may need to run on non-renewable sources which can easily be mitigated with total energy integration approaches.

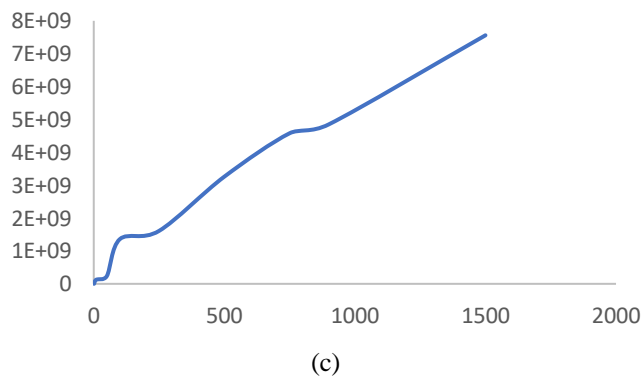
An important recommendation is that the limit of withdrawal needs to be compared with the energy input and output, as well as the net CO₂ cycle, before this process is fully developed.

Biofuels and Biochemicals are not only sustainable, it is a more environmentally-friendly option. In fact, bio-ethanol use decreased greenhouse gas emissions by over 20% in recent years, biodiesel decreases greenhouse gas emissions by 40% to 60%, meaning that the use of biochemicals has already cut 75.5 million metric tons of carbon pollution.

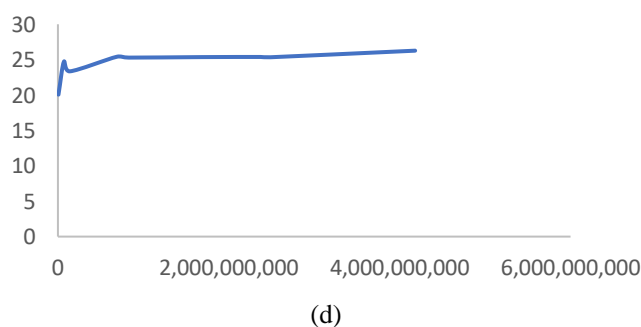
NPV vs Capital Cost



NPV vs Feed Rate



IRR vs Capacity



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