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HYDROPROCESSING OF MICROALGAE OIL FOR GREEN DIESEL PRODUCTION

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ABSTRACT

This research was carried out to simulate microalgae oil hydroprocessing plant using ASPEN HYSYS simulation package. The simulation is based on conditions and parameters (temperature, pressure and catalyst selectivity) obtained from consulted literatures. After the successful completion of the simulation, total recovery of products for green diesel and propane was achieved as 85.6% and 4.01% (mass percentages) respectively. The green diesel composition indicated 0.01, 0.0005, 0.0201, 0.0757, 0.0021, 0.0089, 0.0041, 0.1813, 0.6822, 0.0191, and 0.005 mass fractions of n-C_{15}, n-C_{16}, n-C_{17}, n-C_{18}, n-C_{21}, i-C_{15}, i-C_{16}, i-C_{17}, i-C_{18}, i-C_{21} and H_2O respectively. The quality specifications of the simulated Green diesel with Cetane number 86.7 fall within acceptable range and met the United State diesel standard ASTM D975. A complete disappearance of triglycerides in the product mixture at the hydrotreating temperature of 371 °C and pressure of 20 bar was observed. Economic analysis of the simulated project gives a total capital cost of ? 5.184billion, total production cost of ? 5.01 billion and cash flow as revenue of ? 6.02 billion after the fourth year. It shows that the project is highly profitable and efficient with a pay-back period of approximately 4years.

Keywords — Biofuel, Green diesel, Hydro processing, Microalgae oil, Simulations

INTRODUCTION

Due to increase in human population and further industrialization, energy shortages are becoming the biggest challenge that our society will face in near future (Gerardo et al, 2014). Fossil fuels have been the main source of energy to our hydrocarbon driven society, and the use of these fossil fuels give rise to the production of CO_2, a greenhouse gas known to be directly associated with global warming (Cheng and Govinda, 2010). In contrast to fossil fuels, biomass is a renewable energy resource and carbon neutral in principle (Wang et al, 2014).

Algae are the most preferable biomass (raw material) for biofuel production because it involves direct conversion of solar energy to biofuel with little carbon dioxide emission (Nasir et al, 2012). There are two classifications of algae: Macro algae and Microalgae.

Microalgae from previous research work has been proved to be exceedingly rich in oil than any other vegetable oil source, it doesn't require much land for cultivation, and thus the most suitable option for the production of biofuels (Christi, 2007). This can be observed in table 1 which shows the amount of extractable oil from different oil source, per hectare of land used.

Table 1: Comparison of some sources of biofuel

Crop	Oil yield (L/ha)
Soybean	446
Canola	1,190
Jatropha	1,892
Oil palm	5,950
Corn	172
Coconut	2,689
Microalgae (30% oil by weight)	58,700
Microalgae (70% oil by weight)	136,900

Common algae found in Nigeria (*Chlorella, Nitzschia, Botryococcus braunii, Crypthecodinium cohnii, Cylindrothecasp, etc*) have oil levels between 20 and 50%, but high productivities can be reached (Pratoomyot et al, 2005). One of the factors considered in the

APPENDIX

TABLE 1A: Fatty acids composition (percent of total fatty acids) of 10 microalgal species at the exponential phase (Pratoomyot et al, 2005)

Fatty acid	Nitzschia cf. ovalis	Thalassiosira sp.	Tetraselmis sp.	Dictyosphaerium pulchellum	Stichococcus sp.	Chlorella sp.	Scenedesmus sp.	Anacystis sp.	Synechoccus sp.	Synechocystis sp.
Saturated Fatty Acids (SFA)										
14:00	2.67	4.59	1.31	2.38	2.12	1.58	1.12	3.66	25.96	13.34
16:00	13.25	19.61	15.33	12.56	17.61	13.08	5.76	27.6	13.94	5.89
18:00	0.45	0.35	0.43	0.77	0.54	1.23	0.33	1.4	0.58	1.17
Total SFAs	16.37	24.55	17.07	15.71	20.27	15.89	7.21	32.66	40.48	20.4
Monounsaturated Fatty Acids (MUFA)										
16:1n-7	17.12	31.47	3.23	2.11	-	-	1.06	9.28	34.91	16.72
18:1n-9	0.59	0.41	12.25	2.51	2.87	6.68	2.65	4.83	1.7	1.22
18:1n-7	0.33	0.27	2.26	-	1.63	1.21	0.22	4.04	-	-
20:1n-9	-18.04	-	1.12	-	0.15	0.12	0.49	-	-	-
Total MUFAs		32.15	18.86	4.62	4.65	8.01	4.42	18.15	36.61	17.94
Polyunsaturated Fatty Acids (PUFA)										
16:2n-4	2.45	7.45	4.51	3.06	0.19	-	1.24	-	-	1.96
16:3n-4	7.2	2.84	0.35	0.69	-	9.56	0.92	0.35	0.15	-
18:2n-6	0.43	2	9.66	7.76	14.78	17.54	4.67	1.6	1.46	-
18:3n-3	0.37	1.1	16.17	26.49	25.71	20.02	20.79	23.18	-	-
18:4n-3	-	2.15	1.8	1.84	-	-	2.52	-	-	-
20:4n-6	4.4	0.12	0.99	-	-	-	-	-	-	-
20:4n-3	-	0.16	0.16	-	-	-	-	-	-	-
20:5n-3	26.67	16.65	4.7	-	-	-	-	-	-	-
22:5n-3	0.28	-	-	-	-	-	-	-	-	-
22:6n-3	4.2	1.33	-	-	-	-	-	-	-	-
Total PUFAs	46	33.8	38.38	39.84	40.68	47.12	30.14	25.13	1.61	1.96
Total HUFAs	35.55	18.26	5.85	-	-	-	-	-	-	-

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TABLE 1A: Fatty acids composition (percent of total fatty acids) of 10 microalgal species at the exponential phase (Pratoomyot et al, 2005)

Fatty acid	Nitzschia cf. ovalis	Thalassiosira sp.	Tetraselmis sp.	Dictyosphaerium pulchellum	Stichococcus sp.	Chlorella sp.	Scenedesmus sp.	Anacystis sp.	Synechoccus sp.	Synechocystis sp.
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18:00	0.45	0.35	0.43	0.77	0.54	1.23	0.33	1.4	0.58	1.17
Total SFAs	16.37	24.55	17.07	15.71	20.27	15.89	7.21	32.66	40.48	20.4
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16:1n-7	17.12	31.47	3.23	2.11	-	-	1.06	9.28	34.91	16.72
18:1n-9	0.59	0.41	12.25	2.51	2.87	6.68	2.65	4.83	1.7	1.22
18:1n-7	0.33	0.27	2.26	-	1.63	1.21	0.22	4.04	-	-
20:1n-9	-18.04	-	1.12	-	0.15	0.12	0.49	-	-	-
Total MUFAs		32.15	18.86	4.62	4.65	8.01	4.42	18.15	36.61	17.94
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16:3n-4	7.2	2.84	0.35	0.69	-	9.56	0.92	0.35	0.15	-
18:2n-6	0.43	2	9.66	7.76	14.78	17.54	4.67	1.6	1.46	-
18:3n-3	0.37	1.1	16.17	26.49	25.71	20.02	20.79	23.18	-	-
18:4n-3	-	2.15	1.8	1.84	-	-	2.52	-	-	-
20:4n-6	4.4	0.12	0.99	-	-	-	-	-	-	-
20:4n-3	-	0.16	0.16	-	-	-	-	-	-	-
20:5n-3	26.67	16.65	4.7	-	-	-	-	-	-	-
22:5n-3	0.28	-	-	-	-	-	-	-	-	-
22:6n-3	4.2	1.33	-	-	-	-	-	-	-	-
Total PUFAs	46	33.8	38.38	39.84	40.68	47.12	30.14	25.13	1.61	1.96
Total HUFAs	35.55	18.26	5.85	-	-	-	-	-	-	-

selection of any micro algae specie is the composition of fatty acids, as they have a significant effect on the characteristics of the biofuel produced (Afzaal, 2006)

Existing technology for producing diesel fuel from plant oils such as rapeseed, soybean and palm has largely centred on trans esterification of oils with methanol to produce fatty acid methyl esters (FAME) or biodiesel (Rogelio et al, 2012)

However, there is quality issues associated with its widespread use which include; poor storage stability, low value by-product glycerol, saponification reaction with the caustic present as a catalyst etc. (Andreas and Nikolas, 2013). Thus, another option of biofuel production is a direct hydro treating of non-food triglyceride resources or vegetable oil to form C_{15}-C_{18} hydrocarbons. These processes can be performed using existing petroleum refineries (Marker, 2005). Hydro processing involves hydro treating to remove heteroatoms (sulphur, nitrogen, oxygen) and hydrocracking to saturate and break C–C bonds by reacting oil with hydrogen in the presence of catalyst so as to produce high quality diesel and gasoline molecules (Krar, 2007).

The industrial application of this technology is not yet as common as it happens with biodiesel. Universal Oil Products (*UOP*) and *Ente Nazionale Idrocarburi* (*ENI*) or national hydrocarbons authority, cooperated for the construction of a green diesel production plant in Italy, which processes 0.32 million tons per year of vegetable oils (Holmgreen, 2007).

Krar et al (2007) hydrotreated sunflower oil at 300-450°C using sulphide NiMo/Al_2O_3 catalyst and concluded that the carbon molar yield of straight chain C_{15}-C_{18} alkanes was 71% on a carbon basis, for hydrotreating of pure vegetable oil under optimal reaction conditions.Holmgreen et al (2007) in their research, obtained renewable green diesel by hydrotreating jatropha oil at standard hydrotreating conditions of 270 – 300°C, 2MPa with Pt/H-ZSM-5 and rhenium-modified Pt/H-ZSM-5 catalyst. Rhenium-modified Pt/H-ZSM-5 catalyst were found to be more effective for hydrotreating jatropha oil even at high oil/catalyst ratio of 10, and 80% conversion and 70% selectivity to C_{18} were achieved.

This paper is aimed at hydroprocessing reaction pathways for conversion of microalgae oil to green diesel by modelling the full reactions mechanism and simulating the production process using available data in Aspen HYSYS version (2010). Also, Economic analysis will be conducted on the simulated green diesel process plant with the aid of ICARUS program available in Aspen HYSYS version 10.

MATERIALS AND METHODS

Green Diesel Process Technology: Hydrotreating Process

To enable us model reaction pathways for vegetable oil (triglyceride) conversion to green diesel, we assumed hydro treatment of Microalgae oil. The scope will be limited to the use of the software to demonstrate how a hydro processing unit can be created and tested virtually, based on the data obtained from experiments published in the literature. Aspen Plus was used for the simulation to run and test the proposed hydro processing reactions. The major fatty acids in Microalgae oil are Oleic, Linoleic, Palmitic and Stearic acid, which are shown in Table **1A** in appendix. However, we approximated the Triacylglycerol's (TAGs) content to reflect only the major fatty acids found in Microalgae oil in order to allow us get their exact chemical properties for simulation purpose. The fatty acid of the triglyceride structure is either monounsaturated, polyunsaturated, or saturated, with variable amount of double bonds present (Pratoomyot et al, 2005).

The deoxygenation of triglycerides can follow three different reaction pathways – hydro deoxgenation, decarboxylation and decarbonylation (Rogelio, et al. 2012). The distribution of hydrocarbons in the products is affected by the oxygen elimination route according to the following reactions:

1. Model Hydrodeoxygenation Reaction Pathways

The proposed hydro deoxygenation reactions of Trioleic, Trilinoleic, Tripalmitic, Tristreatic and free fatty acids where oxygen is removed in the form of water are as follows:

Trioleic acid glyceride (18:1)

$$C_{57}H_{104}O_6 + 15H_2 \rightarrow 3n\text{-}C_{18}H_{38} + C_3H_8 + 6H_2O \quad (1)$$

Trilinoleic acid glyceride (18:2)

$$C_{57}H_{98}O_6 + 18H_2 \rightarrow 3n\text{-}C_{18}H_{38} + C_3H_8 + 6H_2O \quad (2)$$

Tristearic acid glyceride (18:0)

$$C_{57}H_{110}O_6 + 12H_2 \rightarrow 3n\text{-}C_{18}H_{38} + C_3H_8 + 6H_2O \quad (3)$$

Tripalmitic acid glyceride (16:0)

$$C_{51}H_{98}O_6 + 12H_2 \rightarrow 3n\text{-}C_{16}H_{34} + C_3H_8 + 6H_2O \quad (4)$$

Free fatty acid as oleic acid

$$C_{18}H_{34}O_2 + 4H_2 \rightarrow n\text{-}C_{18}H_{38} + 2H_2O \quad (5)$$

1. Model Decarboxylation Reaction Pathways

The decarboxylation reactions of trioleic, trilinoleic, tripalmitic, tristreatic and free fatty acids, where oxygen is removed in the form of carbon dioxide (CO_2), are as follows:

Trioleic acid glyceride (18:1)

$$C_{57}H_{104}O_6 + 6H_2 \rightarrow 3n\text{-}C_{17}H_{36} + C_3H_8 + 3CO_2 \quad (6)$$

Trilinoleic acid glyceride (18:2)

$$C_{57}H_{98}O_6 + 9H_2 \rightarrow 3n\text{-}C_{17}H_{36} + C_3H_8 + 3CO_2 \quad (7)$$

Tristearic acid glyceride (18:0)

$$C_{57}H_{110}O_6 + 3H_2 \rightarrow 3n\text{-}C_{17}H_{36} + C_3H_8 + 3CO_2 \quad (8)$$

Tripalmitic acid glyceride (16:0)

$$C_{51}H_{98}O_6 + 3H_2 \rightarrow 3n\text{-}C_{15}H_{32} + C_3H_8 + 3CO_2 \quad (9)$$

Free fatty acid as oleic acid

$$C_{18}H_{34}O_2 + H_2 \rightarrow n\text{-}C_{17}H_{36} + CO_2 \quad (10)$$

2. Model Decarbonylation Reaction Pathways

The decarbonylation reactions of trioleic, trilinoleic, tripalmitic, tristreatic and free fatty acids where oxygen is removed in the form of carbon monoxide (CO) and water are:

Trioleic acid glyceride (18:0)

$$C_{57}H_{104}O_6 + 9H_2 \rightarrow 3n\text{-}C_{17}H_{36} + C_3H_8 + 3CO + 3H_2O \quad (11)$$

Trilinoleic acids glyceride (18:2)

$$C_{57}H_{98}O_6 + 12H_2 \rightarrow 3n\text{-}C_{17}H_{36} + C_3H_8 + 3CO + 3H_2O \quad (12)$$

Tristearic acids glyceride (18:0)

$$C_{57}H_{110}O_6 + 6H_2 \rightarrow 3n\text{-}C_{17}H_{36} + C_3H_8 + 3CO + 3H_2O \quad (13)$$

Tripalmitic acids glyceride (16:0)

$$C_{51}H_{98}O_6 + 6H_2 \rightarrow 3n\text{-}C_{15}H_{32} + C_3H_8 + 3CO + 3H_2O \quad (14)$$

Free fatty acid as oleic acid

$$C_{18}H_{34}O_2 + 2H_2 \rightarrow n\text{-}C_{17}H_{36} + CO + H_2O \quad (15)$$

Other side reactions during the conversion process are water gas shift and methanation reactions.

$$12CO_2 + 12H_2 \leftrightarrow 12CO + 12H_2O \quad (16)$$

$$12CO + 36H_2 \leftrightarrow 12CH_4 + 12H_2O \quad (17)$$

The product distribution is influenced by the reaction pressure. At a high hydrogen pressure, the hydrodeoxygenation reaction will be the favoured reaction pathway. On the other hand, at lower hydrogen pressure, decarboxylation or decarbonylation reaction will be enhanced (Krar, 2007). The selectivity of the catalyst favours the production of the desired products and hinders the side reactions (Rogelio et al; 2012).

Process Simulation

Process simulation allows us to predict the behaviour of a process by using basic engineering relationships, such as mass and energy balances as well as phase and chemical equilibrium (Aspen, 2009). Given reliable thermodynamic data, realistic operating conditions, and rigorous equipment models, we can simulate actual plant behaviour. Process simulation enabled us to run many cases, conduct "what if" analyses, and performed sensitivity studies and optimization runs. With simulation, we can design better plants and increase profitability in existing plants. Process simulation is useful throughout the entire lifecycle of a process, from research and development through process design to production. Aspen Plus makes it easy to build and run a process model by providing a comprehensive system of online prompts, hypertext help, and expert system guidance at every step. Aspen Plus was used to simulate the hydro processing model for conversion of Microalgae oil to biofuel.

Process Flow Diagram of the Green Diesel Process

To represent the green diesel process in Aspen HYSYS, the following procedure was followed:

I. Selection of the appropriate

thermodynamic/fluid package. In the simulation basic manager (basis environment), extended None-Random Two-Liquid (NRTL) was selected as the thermodynamic fluid package as it can handle hydrocarbon, gas components, and liquid mixtures.

II. Selection of all component involved in the process, either in the feed, product or by-product.

III. Defining the reaction stoichiometry.

IV. Construction of the process flow diagram (PFD)

Figure 1 show clearly the process simulation steps which indicate that the simulation result will normally be presented in Hysys spread sheet at the end.

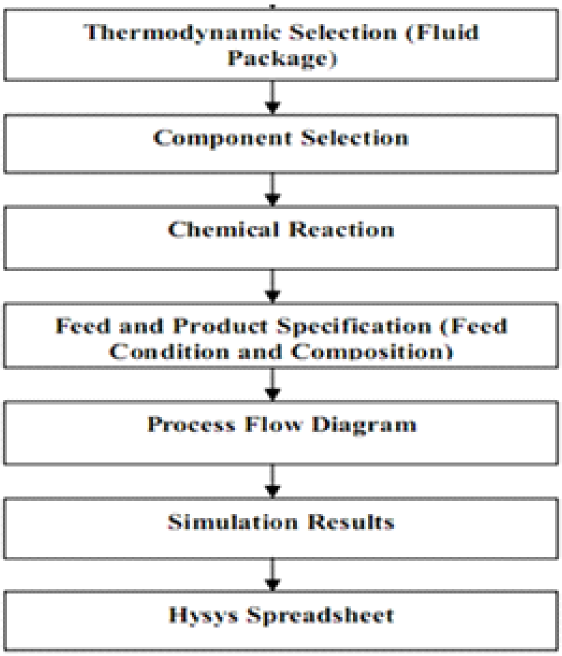

Figure 1: Process Simulation Steps using HYSYS

Process Description

The vegetable oil hydroprocesssing flow diagram simulated using Aspen HYSYS is shown in Figure 2. Microalgae oil from its storage drum is pumped using the feed pump (P-100). It is heated and mixed with pressurized hydrogen stream before feeding into the reactor (HDO reactor). The heat energy of the liquid product stream from HDO reactor is utilized in heating the microalgae oil before the liquid stream is sent to the cooler. The essence of the cooling is to reduce the temperature of the

cooling is to reduce the temperature of the

reactor product to aid separation of unreacted hydrogen, CO, CO_2, and other light ends from the liquid product.

The cooled stream is sent into a two phase separator to separate the unreacted H2 and vapour by-products from the main liquid product. The liquid product from the separator which contains the n-alkanes is sent to the isomerization reactor to convert it from straight chain hydrocarbons to their corresponding isomers, to achieve better cold flow properties of the produced green diesel. Both the HDO reactor and the isomerization reactor were modelled as a conversion reactor. Vapours from the separator and isomerization reactor are sent to the absorber where with the aid of a solvent (selexol), the CO and CO_2 present in the absorber feed stream are absorbed to produce a propane-rich product.

The liquid product from the isomerization reactor is composed of water and other components of green diesel. To obtain a water-free diesel product, the liquid product is sent to a distillation column where the water content is distilled off and the green diesel obtained as the bottom product.

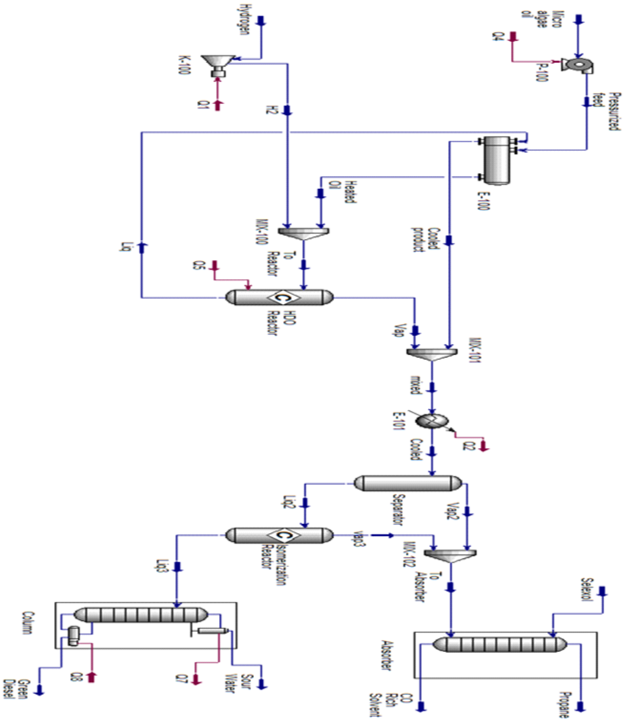

FIGURE 2: Simulated flow diagram of green diesel production process

RESULTS AND DISCUSSION

Hydroprocessing Simulation Result

The hydroprocessing model and simulation framework developed in Aspen HYSYS version 10 was used to convert microalgae oil to green diesel and propane by fitting the reaction parameters obtained from literature. Table 3 shows the composition data of the main feed (Microalgae and Hydrogen) and product streams (Propane and Green diesel) generated from the simulated green diesel process.

The operating temperature and pressure of the reaction section of the simulated green diesel plant are 371^{O}C and 1995kPa (20bar) respectively. At this condition within the hydrodeoxygenation reactor, the glyceride bond of the triglyceride is broken to free the bonded fatty acids. The fatty acids are further hydrogenated through the different pathways of decarbonylation, decarboxylation, and hydrodeoxygenation depending on the selectivity of the catalyst used.

Since the desired result is the production of green diesel and no other lighter ends, product from the HDO reactor is sent to an isomerization reactor with same operating condition as the HDO reactor where the n-alkanes where converted to their corresponding isomers. Assuming the use of zeolite catalyst whose selectivity yields more of C_{18} hydrocarbons and complete conversion of the fatty acid, the hydrotreating microalgae plant was simulated. From Table 3, the flow rate of green diesel is 3891 kg/hr and that of Propane is 201.4 kg/hr as compared to the input mass flow rate of

TABLE 3: Properties of major feed and product streams

Properties	Microalgae Oil	Hydrogen	Propane	Green Diesel
Mass Flow (Kg/hr)	4536	135	201.4	3891
Std Lqd Density (Kg/m3)	913.6	69.86	501.2	759.2
Volumetric flow (m3/hr)	4.965	1.932	0.4018	6.245
Viscosity (cP)	2.89	0.0087	0.0099	0.3011

Table 4 represents the composition of the feed and product streams of the simulated green diesel plant. It shows that all fatty acids present in the microalgae oil feed were completely converted to the main product (green diesel) and the by-product (propane). The green diesel stream comprises of hydrocarbon isomers i-C_{15}, i-C_{16}, i-C_{17}, i-C_{18}, i-C_{21} with mass percentages of 0.89%, 0.41%, 18%, 68% and 1.9% respectively; n-alkanes C_{15}, C_{16}, C_{17}, C_{18}, C_{21} with mass percentage 0.1%, 0.05%, 2.0%, 7.6% and 0.2% respectively, and little composition of water. Computing the percentage sum of the hydrocarbon gives a green diesel yield of 99.15% purity. Similarly, percentage purity of the by-product (propane) from table 3 is 98.88%.

TABLE 4: Composition of the feed and product streams

Components	Microalgae Oil	Hydrogen	Selexol	Propane	Sour Water	Co_2 Extract	Green Diesel
Palmitic Acid	0.0089	0	0	0	0	0	0
Linolenic Acid	0.0021	0	0	0	0	0	0
Palmitoleic Acid	0.0058	0	0	0	0	0	0
Linoleic Acid	0.0115	0	0	0	0	0	0
Oleic acid	0.0236	0	0	0	0	0	0
Stearic Acid	0.0021	0	0	0	0	0	0
n-C4Stearate	0.0209	0	0	0	0	0	0
DiC4Sebacate	0	0	0	0	0	0	0
C19oic Acid	0	0	0	0	0	0	0
Triolein	0.9251	0	0	0	0	0	0
Propane	0	0	0	0.9888	0.0181	0.0090	0
CO2	0	0	0	0	0.0030	0.3099	0
CO	0	0	0	0	0.0001	0.3176	0
H2O	0	0	0	0.0066	0.9775	0.0230	0.0050
Hydrogen	0	1	0	0.0021	0	0	0
n-C15	0	0	0	0	0.0002	0	0.0010
n-C16	0	0	0	0	0	0	0.0005
n-C17	0	0	0	0	0.0004	0	0.0201
n-C18	0	0	0	0	0.0008	0	0.0757
n-C21	0	0	0	0	0	0	0.0021
i-C15	0	0	0	0	0	0	0.0089
i-C16	0	0	0	0	0	0	0.0041
i-C17	0	0	0	0	0	0	0.1813
i-C18	0	0	0	0	0	0	0.6822
i-C21	0	0	0	0	0	0	0.0191
Selexol	0	0	1	0.0007	0	0.3404	0
Methane	0	0	0	0.0018	0	0	0

The Green diesel characterization properties equivalent to petroleum diesel, such as, API gravity, Specific gravity, Flash point, Heating value and Cetane number derived using Aspen Plus properties (Prop-Sets), APISTD, SGSTD, FLPT-API, QVALNET and CETANENO, respectively are presented in Table 5. The quality specifications of simulated Green diesel as compared to standard Green diesel and Petro diesel fall within acceptable range. Therefore, from a refiner's perspective, this simulated green diesel could be considered a premium diesel blending component. The boiling range (287.2°C) is comparable to typical diesel with substantially higher Cetane (86.71) and lower density. These are very valuable properties that enable refiners to optimize the amount of lower value refinery streams that can be blended into refinery diesel pool while meeting the United State diesel standard ASTM D975 (No. 2, boiling range 180 –340°C.)

TABLE 5: Diesel fuel properties

Fuel Properties	Petroleum Diesel	Green diesel (Standard)	Green diesel (Simulated)
% Oxygen	0	0	0
Cloud Point (oC)	-5	-5 to +10	-6.01
Flash Point (oC)			
FLPT-API	60-80	100-170	97.07
Cetane Number			
CETANENO	40	70-90	86.71
APISTD	41.1	45-60	54.7
Distillation (oC)	200-350	265-320	287.2
Heating Value (MJ/kg)			
QVALNET	43	44	45
Specific Gravity SGSTD	0.84	0.78	0.76
Stability	Good	Good	Good

Capital Cost of Project

Economic analysis was conducted on the simulated green diesel process plant with the aid of ICARUS program available in Aspen HYSYS version 8. The ICARUS program is meant for economic evaluation and investment analysis for any simulated process plant on the HYSYS environment. Table 6 summarises the plant capital cost, with the total project cost of $31.42million (? 5.184billion). The largest share of the cost is incurred in purchased equipment of $19,363,957.50 (? 3,195,052,988.00) and the least cost of $129,211.80 (? 21,319,947.50) is spent on steel, while subcontracts and escalation costs are assumed to be zero. The Dollar exchange rate is kept at $1 = ? 165.

TABLE 6: Summary of Plant Capital Cost

PROJECT CAPITAL	TOTAL COST (USD, $)	NAIRA EQUIVALENT (□)
Purchased Equipment	19,363,957.50	3,195,052,988.00
Equipment Setting	152,710.80	25,197,150.00
Piping	967,213.00	159,590,145.00
Civil	292,475.40	48,258,441.00
Steel	129,211.80	21,319,947.50
Instrumentation	1,530,000.00	252,450,000.00
Electrical	1,096,440.00	180,912,600.00
Insulation	406,363.00	67,049,895.00
Paint	130,116.70	21,469,255.50
Other	3,090,000.00	509,850,000.00
Subcontracts	0	0.00
G and A Overheads	585,150.00	96,549,750.00
Contract Fee	1,094,007.00	180,511,155.00
Escalation	0	0.00
Contingencies	2,580,000.00	425,700,000.00

Operating Cost of Project

Operating cost comprises the cost of raw materials, labour cost, utility cost, operating charges, plant overhead, general and administrative (G & A) cost.

The raw materials used for this project with their respective cost are:

Microalgae oil at □ 38.94/lb.(Christi, 2007)

Hydrogen gas at □ 52.80/lb. (Carmo et. al., 2013)

Selexol at □ 217.80/lb. (buckler and schendel, 1984)

Table 7 shows the total operating cost of $30,342,695.00 (□5,006,544,675.00), with the highest cost of $25,900,000 (□4,273,500,000) spent on the purchase of raw material and the least cost of $252,023 (□41,583,795) is incurred on operating charges.

TABLE 7: Summary of Operating Cost

OPERATING COST SUMMARY	COST/PERIOD (USD)	NAIRA EQUIVALENT (□)
Total Raw Material Cost	25,900,000.00	4,273,500,000.00
Total Operating Labour and Maintenance Cost	1,111,091.00	183,330,015.00
Total Utilities Cost	274,036.00	45,215,940.00
Operating Charges	252,023.00	41,583,795.00
Plant Overhead	555,545.00	91,664,925.00
G and A Cost	2,250,000.00	371,250,000.00
Total Operating Cost	**0,342,695.00**	**5,006,544,675.00**

Raw Material Cost: This makes up the cost of all the raw materials used in producing the desired green diesel product. Table 8 is a summary of raw material cost which shows a total of $25,895,394 (? 4,272,740,066.10) and this corresponds to the amount listed in Table 7.

The highest cost of $20,600,594 (? 3,399,098,066.10) is incurred in the supply of Microalgae oil, while the least cost of $1,735,713 (? 286,392,694.50) is spent on the supply of Selexol solvent.

Table 8: Summary of Raw Material

Raw Material	Mass Flow rate (lb/hr)	Cost per hour (USD)	Cost per Annum (USD)	Cost per Annum (□)
Hydrogen	290	406.01	3,559,087	587,249,305.50
Microalgae Oil	10,000	2350.06	20,600,594	3,399,098,066.10
Selexol	150	198.01	1,735,713	286,392,694.50
TOTAL			**25,895,394**	**4,272,740,066.10**

Revenue from Product Sales

The total revenue derived from sales of product produced is tabulated in table 9. Based on the assumption that green diesel will cost same price with petroleum diesel, the main product, green diesel will be sold at $0.725/Ib (□119.63/lb) and the by-product, propane, will sale at □173.25/lb (www.indexmundi.com,2014). The total sum of $54,408,182 equivalent to □8,977,350,001.95 will be generated per annum as sales revenue from green diesel and the by-product propane will generate revenue of $3,463,656, equivalent to □571,503,198.42 per annum. The used selexol solvent will be sold at a high cost of $3,687,355.70 (□608,413,690.50) per annum. Generally, a total product sale of $61,559,193 (□10,157,266,890.87) will be attained annually.

TABLE 9: Summary of Product Sales

PRODUCT	Mass Flow rate (lb/hr)	Mass Flow rate (Barrel/day)	Unit Cost (USD/lb)	Cost per Annum (USD)	Cost per Annum (□)
Green Diesel	8,560.92	772.2	0.725	54,408,182	8,977,350,001.95
Propane	400.61	-	1.05	3,463,656	571,503,198.42
Used Solvent	493.9	-	0.8	3,687,355.70	608,413,690.50
Total Product Sales				**61,559,193**	**10,157,266,890.87**

Profitability Analysis

TABLE 10: Revenue analysis for the first six years as extracted from results generated

PARAMETER	USD/Yr.1	USD/Yr.2	USD/Yr.3	USD/Yr.4	USD/Yr.5	USD/Yr.6
Revenue	-13521800	18418484	19642184	20952564	22205440	23767590
DEP	709276	709276	709276	709276	709276	709276
EBT	-14249500	17632560	18905390	20230602	21581390	23086900
TAX (Taxes)	0.00	7093020	7572150	8084241	8613240	91834780
NE	-14243500	10639795	11426323	12146360	12948820	13852181
TED	-13221800	11328684	12152184	12945256	13620544	14597675
TEX	19494700	17633700	18508900	19215610	19843060	20517144
CF	-13521800	11328684	12152184	12945256	13620544	14597675

Where:

DEP = Depreciation

EBT = Earnings before Tax

NE =Net Earnings (Profit after Tax)

TED =Total Earnings

TEX = Total Expenses, Excluding Tax and Depreciation

CF = Cash Flow for Project

Yr. = Year

Table 11: Summary of Project Profitability Analysis

PARAMETER	
NPV (Net Present Value)	Negative for the first 4 years and Positive for the rest life span
IRR (Internal Rate of Return)	58.22%
MIRR (Modified Internal Rate of Return)	23.28%
NRR (Net Return Rate)	31.3%
PO (Payout Period)	4.1years
ARR (Accounting Rate of Return)	135.81
PI (Profitability Index)	1.31

Table 10 and 11 shows the profitability analysis of the project for the first six consecutive years. The cash flow in the first year with a negative value shows that loss will be encountered for the first production year. Profits will be incurred from the second year as observed from the cash flow. Addition of the cash flows from the first year towards downwards gives a value of $36.52million (□6.02billion) just after the fourth year, which shows that the actual years i.e. pay-back period required to realize the capital ($31.4million) invested in the project is 4.1years

CONCLUSION

In this work, seventeen hypothetical hydro processing reaction steps or pathways have been modelled. C17 and C18 hydrocarbons make up more than 85% of total major product alkanes and C18 hydrocarbon yield is 2.5 times more than C17 hydrocarbon yield. This indicates that hydro deoxygenation route (which forms C18 hydrocarbon) is much favoured than decarboxylation/decarbonylation route (which forms C17 hydrocarbon.) Green diesel is the major product formed with a total flow of 3,891 kg/hr and the straight chain alkanes ranging from C5 to C18 are the majority of products produced during hydro processing reaction. The quality specifications of the simulated green diesel with Cetane number 86.71, oxygen content 0%, heating value 45 MJ/kg, boiling range 287.2°C as compared to standard green diesel and petro diesel with Cetane number 40, oxygen content 0%, and heating value 43 MJ/kg fall within acceptable range. These are very valuable properties that enable refiners to optimize the amount of lower value refinery streams that can be blended into refinery diesel pool while meeting the United State diesel standard ASTM D975 (No. 2, boiling range 180 –340°C.) Therefore, from a refiner's perspective, this simulated green diesel could be considered a premium diesel blending component.

The use of Aspen-Plus as a simulation software package has been tested by studying the effect of the process variables on product yields or throughput and found to be effective. Hence, hydro processing of vegetable oil (triglyceride) has a prospective to become a vital process for the production of biofuels since it offers high-quality hydrocarbon-based fuels. Percentage purity of green diesel and propane was achieved as 99.15% and 98.88% respectively. Percentage product recovery of 89.6% (mass percentage) was achieved with 85.6% of the microalgae oil converted to green diesel and 4.01% of the oil converted to propane. Economic analysis of the simulated project shows that the project is highly profitable and efficient with a pay-back period of approximately 4years. It is recommended to test the process at a pilot plant to better simulate real-plant conditions.

RECOMMENDATION

Kinetics of fatty acids hydrotreating should be investigated to aid further simulation of the process plant using kinetic reactors such as continuous stirred tank reactor (CSTR) and plug flow reactors (PFR)

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