

Sequential Production of Methyl-ester, Bioethanol and Briquette from SCG

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Submitted: 16 Aug 2018; Accepted: 24 Aug 2018; Published: 04 Oct 2018

Abstract

In this study, methyl-ester, bioethanol and briquette samples were sequentially produced from spent coffee ground. The oil extracted from spent coffee ground with solvent extraction route at hexane to spent coffee ground ratio of 22.5g/g with an extraction time of 30.4min resulting in 11.892% of oil yield. This was comparable with literature values and subsequently used for methyl-ester production experiments using a 1% by wt of NaOH at reaction temperatures and residence times ranging from 50 to 65 °C and 20 to 60min, respectively. The optimization carried out using central composite design methodology gave 81.507% of methyl-ester yield at a reaction temperature of 57.133°C and reaction time (residence time) of 45.117 min with model determination coefficient (R^2) of 0.9465 while the optimum reducing sugar yield for dilute acid hydrolysis experiments for ranges of operating parameters of temperature (70-100°C) and (1-3M) of H_2SO_4 concentrations was found to be 39.161% at a temperature of 98.313°C and H_2SO_4 acid concentration of 2.962M. The central composite design optimization results for trans-esterification and dilute acid hydrolysis experiments were verified by running experiments at optimum conditions and in turn resulted 79.65% of Methyl Ester yield (out of 11.892g of oil) and reducing sugars yield of 37.28% (out of the hydrolysate). This implied that the verification experimental results weren't far from the predicted values so that the experimental results were sufficiently represented by the central composite design models. The bio ethanol produced by simple distillation having alcohol by volume yield of 55% can be considered as a good result and it can be easily concentrated to a fuel grade ethanol by using fractionating column. Moreover, the characteristics of the Methyl Ester produced were in good agreement with ASTM and EN standards. The end product of the process which is briquette has been produced from 75% wt of dilute acid hydrolysis residue and 25% wt of glycerol, resulted a calorific value of 13.35MJ/kg, volatile matter value of 88.15%, ash content of 3.95%, and fixed carbon contents of 1.74% with its easily moldable physical status showed that it can as well be used for fueling purpose like firewood and charcoal. This study signifies the value addition that can be affected from spent coffee ground and the potential and results obtained in this regard are discussed.

Keywords: spent coffee ground, central composite design, alcohol by volume

Abbreviations

SCG- Spent Coffee Ground
DOE-Design of Experiment
ANOVA-Analysis of Variance
CCD-Central Composite Design
RSM-Response Surface Method
2FI-Sequential Sum of Squares for the Two-factor Interaction
ALCs- Akaike's Information Criterion with a correction for a small design.
BIC- stands for Bayesian Information Criterion better for larger designs
Df-Degree of Freedom
HHV-High Heating Value (Calorific value)
FP-Flash Point
SN-Saponification Number
IN-Iodine Number
AV-Acid Value
FFA- Free Fatty Acid
Prob F-Probability Function

p-value- is the standard method looking for significant terms
VM-Volatile matter
FC-Fixed carbon
ASTM-American Society for Testing and Materials
EN- European Standards
ABV-Alcohol by Volume

Introduction

Coffee is the most important agricultural commodity in the world and is second only to petroleum in global trade activity and value [1]. According to the International Coffee Organization, about 120 million bags of coffee are produced annually worldwide, corresponding to over 7 million tons of coffee beans per year. Of the several species in the genus *Coffea* (Rubiaceae), only *Coffea arabica* and *Coffea canephora* var. *robusta* are cultivated for commercial production. They are commonly referred to as Arabica and Robusta, with the former accounting for 70 to 75% of the total production [2,3]. Arabica is grown at altitudes over 1000 m and is considered to be of superior quality because of the milder and more flavorful taste developed by the beans during roasting [4]. The Robusta variety is mostly used by the instant coffee industry for producing soluble coffee extracts [5]. During the preparation of a coffee beverage or

the manufacturing of instant coffee, raw coffee powder is contacted with hot water or steam under conditions favoring the release of aroma compounds and other coffee-bean constituents into the liquid. From these operations, a solid residue known as spent coffee grounds (SCG) is produced. SCG have no commercial value and are usually discarded as solid waste or, to a very limited extent, sent to compost facilities. In recent years, however, the increasing awareness of the need for waste reduction and environmental protection has stimulated the search for possible methods of using this waste. Most research efforts have been devoted to the direct use of SCG rather than the recovery of potentially valuable components from it. The chemical composition of exhausted coffee waste generated in a soluble coffee industry was investigated. The chemical characterization included elemental analysis, mineral composition and ash content, summative composition; acidic functional groups, lipophilic extractives, total polyphenols, condensed tannins determination and FTIR analysis. The spent coffee samples showed high carbon (>58%), low nitrogen (<2%), and low ash (<1%) contents and low polarity coefficient $(O + N)/C (<0.5)$. The summative composition reveals that extractives are the main components of exhausted coffee wastes (54%), this percentage includes lipophilic fractions (24%), ethanol and water soluble compounds (5%), and compounds solubilized in 1% NaOH (26%) [6,12]. Lignin and polysaccharides were found in a similar proportion between 20 and 26% [6]. The GC analysis of monosaccharide showed about 60% glucose and 40% mannose. The main components in the lipophilic extractives are free fatty acids (>60%) of which more than 30% was identified to be n-hexadecanoic acid. Total polyphenols and tannins represent <6% and <4% of the exhausted coffee wastes, respectively [6]. Assignments of the bands of the obtained FTIR spectra confirm the presence of lipids, polysaccharides and chlorogenic acid. Exhausted coffee wastes showed characteristics for various potential applications such as Methyl Esterproduction, as a source of antioxidants and as a biosorbent of hydrophobic pollutants. Waste coffee grounds contain between 7 – 14 % lipids with a significant glyceride portion that can be trans-esterified into biodiesel. The amount of lipid in the coffee does vary from coffee type though this cannot simplistically attribute to geographic region or the type of bean [6]. The amount of un-saponifiable lipid also varies and can be as high as 40% in some oils. The un-saponifiable lipid is generally less prevalent in the spent coffee than it is in the fresh; this means that similar Methyl Esterproduction levels are achieved for both the fresh and the spent coffee grounds. The FAME profile produced hardly varies irrespective of the region or processing, and contains high levels of palmitic and linolenic acid and lower levels of stearic and oleic acid.

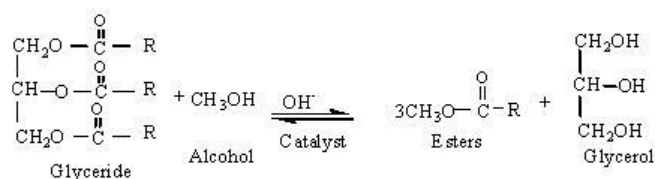
Table 1.0: Constituents of spent coffee ground

Parameters	Values
Moisture (%)	65.7
Total Carbon (% wt)	67.3
Total Nitrogen (% wt)	2.2
Protein (g protein/100 g)	13.7
Ash(% wt)	2.2
Cellulose(% wt)	13.8
Lignin (% wt)	31.9
Soluble Lignin(% wt)	1.7
Total Lignin(% wt)	33.6

Source: Lago et al. (2001); Melo et al. (2007); Bizzo (2003); Nogueira and Costa (1999); Mussatto et al. (2011a); Mussatto et al. (2011b); Bizzo. (2003)

Making of Biodiesel Trans-esterification

Trans-esterification of natural glycerides with methanol to methylesters is a technically important reaction that has been used extensively in the soap and detergent manufacturing industry worldwide for many years. Almost all Methyl Esteris produced in a similar chemical process using base catalyzed Trans-esterification as it is the most economical process, requiring only low temperatures and pressures while producing a 98% conversion yield. The reaction between the fat or oil and the alcohol is a reversible reaction, so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion. A successful Trans-esterification reaction is signified by the separation of the methyl ester (biodiesel) and glycerol layers after the reaction time.



Catalysts Used for Biodiesel Production

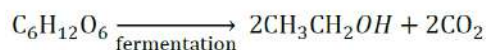
The Trans-esterification reaction is usually carried out in the presence of catalysts. Alkaline, acidic, biological (lipases) or heterogeneous catalysts are usually utilized to improve the Trans-esterification reaction rates for a variety of biomass oils.

Alkaline Catalysts

Sodium Hydroxide (NaOH), Sodium Methoxide (CH₃ONa), Potassium Hydroxide (KOH) and Potassium Methoxide (CH₃OK), are more commonly used for the Trans-esterification of high quality biomass oils. For alkaline alcoholysis, a catalyst concentration (NaOH and KOH) in the range of 0.4-2% w/w (on the basis of the oil weight) was reported to be usually applied for alkyl ester production in research and industry [7].

Overall Process of Bio-ethanol Production

The process of ethanol production depends on the raw materials used. Ethanol production commonly carried out into the major three steps: to obtain the solution containing fermentable sugars, conversion of sugars into ethanol by fermentation and ethanol separation and purification, usually by distillation–rectification–dehydration. One or more steps can be combined depending on the feedstock and the conversion technology. Through the pretreatment, carbohydrates are extracted or made more accessible to the further extraction. The fermentation reactions occur at temperatures between 25°C and 38°C and it last between 6 h and 72 h depending on the composition of the hydrolysate, cell density, physiological activity and yeast species and its reaction is given by the following chemical equation:



Briquetting

Densification essentially involves two parts; the compaction under pressure of loose material to reduce its volume and to agglomerate the material so that the product remains in the compressed state.

The resulting solid is called a briquette if, roughly, it has a diameter greater than 30 mm. Smaller sizes are normally termed pellets though the distinction is arbitrary. If the material is compacted with low to moderate pressure (0.2-5 MPa), the space between particles is reduced. Increasing the pressure will, at a certain stage particular to each material, collapse the cell walls of the cellulose constituent; thus approaching the physical, or dry mass, density of the material. The pressures required to achieve such high densities are typically 100 MPa plus. This process of compaction is entirely related to the pressure exerted on the material and its physical characteristics. The reduction of material density is the reason for undertaking briquetting as it determines both the savings in transport and handling costs and any improvement in combustion efficiency over the original material. The ultimate density of a briquette will depend to some extent on a range of factors including, most importantly, the nature of the original material and the machine used and its operating condition as well as other minor factors. The ultimate limit is for most materials between 1,450 and 1,500 kg/m³. Since the material also will have to be dried in order to facilitate briquetting, the resulting increase in energy content per volume unit can be large compared to the raw materials. A binding agent is necessary to prevent the compressed material springing back to its original form. This agent can either be added to the process or, be a part of the material itself in the form of lignin or sulfuric lignin. At present to main high pressure technologies: ram or piston press and screw extrusion machines are used for briquetting. While the briquettes produced by a piston press are completely solid, screw press briquettes on the other hand have a concentric hole which gives better combustion characteristics due to a larger specific area. The screw press briquettes are also homogeneous and do not disintegrate easily.

The Potential Availability of Spent Coffee Ground

According to the data given by [United States Department of Agriculture] the estimated amount of coffee that will be produced in a year 2017/18 is 392,700 tons of which 50% of the produced coffee 196,350 tons are to be exported and this shows that about 50% of the produced coffee will be consumed locally. From each gram of coffee around 25-28% of extractable constituents are extracted while the remaining 72-75% is to be the SCG. This shows that there is a very high potential for converting the SCG to biofuels. As per Technavio's data it is expected that the global instant coffee market to continue growing. The sale of instant coffee constitutes 40% of the global coffee sales. The global trade of instant coffee grew at an annual rate of 4%, which represented an increase from 360,000 tons in 2005 to 440,000 tons in 2011. Spray-dried products dominated the global instant coffee trade. In 2011, freeze-dried exports were close to 95,000 tons a year, accounting for 23% of the global instant coffee trade. The process of instant coffee production has resulted Avery high amount of spent which contains high percentages of lipids and polysaccharides where aroma and caffeine contents are extracted through the process.

Studies on Lipid Extraction from Spent Coffee Ground and its Biodiesel Potential

Previously, researches on using spent coffee grounds (SCG) for Methyl Esterproduction and other application, an experimental study were conducted with different solvents showing that lipid content up to 6 wt% can be obtained from SCG [9]. Results also show that besides Methyl Esterproduction, SCG can be used as fertilizer as it is rich in nitrogen, and as solid fuel with higher heating value (HHV) equivalent to some agriculture and wood residues. The extracted lipids were characterized for their properties of acid value, density,

viscosity at 40 °C, iodine number, and HHV, which are negatively influenced by water content and solvents used in lipid extraction. Results suggest that for lipids with high free fatty acids (FFA), the best procedure for conversion to Methyl Esterwould be a two-step process of acid esterification followed by alkaline Trans- esterification, instead of a sole step of direct Trans- esterification with acid catalyst. Biodiesel was characterized for its properties of iodine number, acid value, and ester content. Although these quality parameters were not within the limits of NP EN 14214:2009 standard, SCG lipids can be used for biodiesel, blended with higher-quality vegetable oils before Trans-esterification, or the Methyl Esterproduced from SCG can be blended with higher-quality Methyl Esteror even with fossil diesel, in order to meet the standard requirements. The research conducted on optimization of two parameters; oil extraction time and the ratio of dried spent coffee ground to solvent were varied on dried spent coffee grounds employing four solvents [10]. Extracted yields were investigated using response surface method and the two independent parameters were varied in a range (5.1-24.9g/g) for dried spent coffee ground and (0.2-39.8min) for extraction time. After verifying the result using conducting actual experiments, the researcher achieved the following yields for different solvents and they were 14.7 percent by weight (wt%; using hexane), 13.1 wt% (using anhydrous ethanol), 11.8 wt% (using hydrous ethanol), and 7.5 wt% (using methanol). Prototype extraction was tested using a circulation process. Approximately 11.8 wt% oil yield of prototype extraction could be obtained from dried spent coffee ground under the optimal conditions of 30.4 min extraction time and 22.5 g/g ratio of DSCG-to-hexane from the laboratory-scale results.

Studies on Potentials of Spent Coffee Ground as a Solid Fuel (Briquette)

The current policy of waste management requires, above all, a gradual reduction of waste amount and, to a larger extent, forces us to seek new methods of waste disposal. Recycling the energy contained in biomass waste is a more and more universally applied method of thermal converting. Biomass combustion allows saving fossil fuels which fits into sustainable development. Previously conducted research checks the possibility of using spent coffee ground (SCG) in energy recycling using a combustion process [11]. This particular biomass type up to now has not been widely examined, which inclines to consider its usage as a potential additive to alternative fuels. In the study, researchers examined the quality of fuel, which was in a form of briquette, made of beech shavings with 10 and 25% of post-exploitation waste obtained during the process of coffee infusion [11]. This waste, if fresh, is distinguished by its high hydration. However, after drying it may constitute a valuable additive to alternative fuels. It increases the calorific value of fuel and reduces briquettes' hardness what contributes to reducing resistance of conveying screw in stoves.

Table 2.0: Properties of SCG residue after ethanol production

Property		Unit	Values
Gross Calorific Value		MJ/Kg	20.8
Proximate Analysis	Fixed Carbon	Wt%	17.55
	Moisture Content	Wt%	4.5
	Ash	Wt%	2.04
	Volatile Matter	Wt%	75.87
Total Nitrogen		Wt%	2.30
Total Carbon		Wt%	50.43

Material and Methods

Materials and Equipment to Be Used

Spent ground coffee samples will be collected from some cafeterias found in jimma town, and the following materials and chemicals are to be used as well. Digital Vibro viscometer(SV-10 / SV-100), Refractometer(REF-113ATC), autoclave machine(YX280-B), conical flasks, spatula, microwave oven(BP090), hydrometer(1.02-1.892), water bath (IC-TWB-24D-CP) , test tubes, thermometer(lab grade), Continuous stirred tank reactor (CSTR-CEPMKII), Soxhlet Extractor ,distillation flasks, briquetting machine(manual), fermentation flask, pH paper and meter, dry active yeast, yeast extract, potassium diphosphate, calcium chloride, copper II sulphate, nutrients, sodium hydroxide for pH correction, sulphuric acid for hydrolysis, n-hexane for extraction, sodium hydroxide for Transesterification.

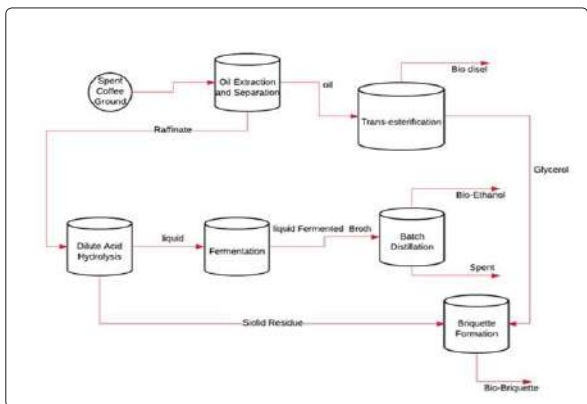


Figure 1.0: Process flow sheet for methyl-ester, bioethanol and briquette production process

Experimental Procedures

Moisture Content Determination

The spent coffee grounds (SCGs) were allowed to air dry for several days and then characterized to evaluate its moisture content by repeated cycles of oven drying at 105 °C followed by cooling in a desiccators over silica gel (0% relative humidity) and weighing until a constant weight. The moisture content was determined as in following Equation;

$$M = \frac{W_1 - W_2}{W_1} * 100 \dots \dots \dots (1)$$

Where M, W1, W2 are moisture content, initial and final weight of the sample

Particle Size for Dried Spent Coffee Ground Samples

The particle size of spent coffee ground sample was determined using vibratory sieves having 2 and 1mm diameter and the sample retained on the 1mm sieve has an average particle size which is between 1mm and 2mm.

Methyl-ester Production

Oil Extraction from Spent Coffee Grounds (SCGs)

According to the research conducted on optimization of oil extraction from spent coffee ground [12] the operating condition chosen for the design were 30.4 min extraction time and 22.5 g/g ratio of dried SCG-to-hexane. In this research the experiments were conducted at two sides of the optimum condition this is to check

the variation. One combination was 25 min extraction time and 17g/g ratio of dried SCG-to-hexane and at 35 min extraction time and 27 g/g ratio of dried SCG-to-hexane and another experiment at the optimum condition given above was conducted. The experiment was conducted in twenty replicates at the maximum yield giving conditions and percentage yield of oil was calculated using the equation below:

$$Y_{oil(\%)} = \frac{W_o}{W_s} * 100 \dots \dots \dots (2)$$

Where: Y_(oil), W_o and W_s are percentage oil yield, weight of oil extracted, and weight of dried spent coffee ground, respectively.



Figure 2.0: Soxhlet extraction of SCG oil

Physio-chemical Characterization of SCGs Oil

Determination of Iodine Value (IV)

The method specified by ISO 3961 (1989) was used. 0.4g of the sample was weighed into a conical flask and 20ml of carbon tetra chloride was added to dissolve the oil. Then 25ml of Dam's (Iodine monochloride) reagent was added to the flask using a safety pipette in fume chamber. Stopper was then inserted and the content of the flask was vigorously swirled. The flask was then placed in the dark place for 2.5 hours. At the end of this period, 20ml of 10% aqueous potassium iodide and 125ml of water were added using a measuring cylinder. The content was titrated with 0.1N sodium-thiosuphate solutions until the yellow color almost disappeared. Few drops of 1% starch indicator was added and the titration continued by adding sodium thiosuphate drop wise until blue coloration disappeared after vigorous shaking. The same procedure was used for blank test and other samples. The iodine value (IV) is given by the expression:

$$I_v = 12.69 * N * \frac{V_2 - V_1}{M} \dots \dots \dots (3)$$

Where, N = normality of sodium thiosuphate, V₁ = Volume of sodium thiosuphate V₂ = Volume of sodium thiosuphate used for blank, M = Mass of the sample the same procedure was used to determine the Iodine value of biodiesel.

Acid and Saponification Values

The AV of the oil was determined using analytical titration method. 25ml of diethyl ether and ethanol mixture was added to 5gm of oil in a 250ml conical flask and the solution was titrated with 0.1N ethanolic KOH solution in the presence of 5 drops of phenolphthalein as indicator until the endpoint (colorless to pink) is recognized with consistent shaking. The volume of 0.1 N ethanolic KOH (V) for the sample titration was recorded. The total acidity of oil in mg KOH/

gram was calculated using the following equation:

$$A_v = \frac{56.1 \cdot N \cdot V}{W} \dots \dots \dots (3)$$

Where: A_v , N , V and W , are acid value of oil, concentration of ethanolic KOH, volume of 0.1N ethanolic KOH solution, the weight of oil sample. Then the percentage free fatty acid value (%FFA) was calculated using the following equation:

$$\%FFA = \frac{A_v}{2} \dots \dots \dots (4)$$

Determination of Saponification Number (SN)

Indicator method was used as specified by ISO 3657 (1988). The SN determination was conducted by dissolving the oil in an ethanolic KOH solution. 2g of the sample was weighed into a conical flask then 25ml of 0.1N ethanolic potassium hydroxide solution was added. The content was constantly stirred, and allowed to boil gently for 60min. A reflux condenser was placed on the flask containing the mixture. Few drops of phenolphthalein indicator was added to the warm solution and then titrated with 0.5M HCl (volume V_a was recorded) to the endpoint until the pink color of the indicator just disappeared. Then a blank determination was carried out upon the same quantity of potassium hydroxide solution at the same time and under the same conditions and (volume V_b was recorded). The result was calculated using equation:

$$S_N = \frac{56.1 \cdot N \cdot (V_b - V_a)}{W} \dots \dots \dots (5)$$

Where W = weight of oil taken in gram, N = normality of HCL solution, V_a = volume of HCL solution used in test in ml, V_b = volume of HCL solution used in blank in ml. The same procedure was used to determine the SN of methyl-ester as discussed above.

Determination of Viscosity (μ)

Digital Vibro viscometer was used to determine the viscosity of oil and methyl-ester. The kinematic viscosity was determined at 40°C followed by ASTM D445-09.

Base Catalyzed Trans-esterification

The extracted SCG oil was used in the trans- esterification reaction where Methanol (Analytical grade) with Mwt. 32.04 and purity of 99.8% and analytical grade NaOH was used as a catalyst. Since the method applied in this study was the alkali-catalyzed trans-esterification. The trans-esterification process was studied at a constant catalyst loading (1.0% NaOH wt./wt.), three reaction temperature ranges (55, 65 and 75°C) and alcohol-to-oil molar ratios (3:1v/v) was used. In the process of trans-esterification process sodium methoxide solution was prepared freshly by mixing a predetermined amount of methanol with NaOH (1.0% by weight of oil) in a container. The reaction was carried out in a range of 20-60 minutes. Stirring (150rpm) was started with the reaction at the moment of sodium methoxide solution. After the predetermined reaction time, the mixture was carefully transferred to a separating funnel and allowed to stand there overnight. The lower layer (glycerol, methanol and most of the catalysts) was drained out. The upper layer (methyl esters, some methanol and traces of the catalyst) was then cleaned thoroughly by washing with warm (50 °C) de-ionized water. The methyl ester was then dried with anhydrous Na_2SO_4 . Biodiesel and glycerol yields were calculated at different combinations of operating parameters and the result was fed to the design expert software where optimization was done using the

Central Composite Method. The following formula was used for the calculations of methyl-ester and glycerol yield.

$$Y_{b(\%)} = \frac{V_b}{V_0} * 100 \dots \dots \dots (5)$$

$$Y_{g(\%)} = \frac{V_g}{V_0} * 100 \dots \dots \dots (5.1)$$

Where: Y_b , Y_g , V_b , V_g and V_0 are percentage yield of methyl-ester and unconverted oil with glycerol, volume of Methyl Ester and glycerol produced and volume of oil used, respectively



Figure 3: Esterified samples



Figure 4: Purified methyl-ester samples

Characterization of Methyl-ester

Physical and chemical properties of SCG Methyl Ester were characterized using some empirical correlation and analytical methods. High Heating Value, saponification value, Flash point, Cetane Number. The Acid, Iodine and Saponification values and viscosity of Methyl Ester were determined with the application of same methods used for oil characterization except change in gram of sample. Determination of Viscosity, High Heating Value, Flash Point and Density of Biodiesel at optimum conditions was done by methods herein below.

Higher Heating Value

Determination of Heating Value (Calorific Value): The HHV of the Methyl Ester was determined using the empirical formula suggested by [13].

$$HHV = 49.3 - [0.041(S_N) + 0.015(I_V)] \dots \dots \dots (6)$$

Cetane Number

The Cetane number of the Methyl Ester was determined using the empirical formula suggested by the research [14], using the result of SN and IV of the biodiesel:

$$C_N = 46.3 + \frac{5458}{S_N} - 0.225(I_V) \dots \dots \dots (6.1)$$

Determination of Flash Point

The FP of the Methyl Ester was determined using empirical formula

by [14]. The equation between FP and HHV for Methyl Esteris:

$$\text{HHV}=0.021\text{FP}+32.12 \dots \dots \dots (6.2)$$

Ethanol Production

Preparation and Sterilization of Growth Media

A semi synthetic broth media will be prepared using the following: potassium diphosphate, ammonium sulphate, calcium chloride magnesium sulphate, iron II sulphate, and yeast extract. All will be dissolved in one liter of distilled water in a conical flask. The solution was then placed into an autoclave at a temperature of 121°C for 15 minutes and at a pressure of 15 psia to destroy any impurity that might inhibit a microorganism in the system and allowed to cool to 40°C before it is brought out of autoclave.

Acid Hydrolysis of Starch in the Raffinate

The raffinate or solid residue of extraction process was collected from the dilute acid hydrolysis process. And it was first washed with distilled water in order to remove the dirty particles from the sample. Then, the sample was weighted and left in the drying oven operating at 105°C for a day. The dried sample of raffinate was weighted to 100g and put in 500ml flask and different molarity of sulfuric acid (1M,2M and 3M) acid was prepared and added (450ml/100g of residue) on the sample while the operating temperatures were set at (90,115, and 140°C) stirred for a constant residence time 30 minutes. Then the mixture was added in glass bottles and sealed to prevent contamination and vaporization of acid due to heat. After hydrolysis the liquid fraction of the hydrolysate samples were filtered, collected, and their sugar content was determined as follows.



Figure 5: Dilute H₂SO₄ preparation



Figure 6: Hydrolysate samples

Fehling method

50 mL of hydrolyzed filtered sample solution was neutralized with 4 M NaOH and 2.5 M HCl and the solution was made up to a volume of 300 mL and taken into the burette. Then, 5 mL of Fehling A (prepared by dissolving 34.6 g of copper (II) sulfate pentahydrate in 500 mL and 5 mL of Fehling B solution's (prepared by dissolving 125 g of potassium hydroxide and 173 g of potassium sodium tartrate tetra

hydrate in 500 mL of distilled water) were taken and mixed with 90 mL of distilled water in 250 mL Erlenmeyer flask and methylene blue indicator was added.



Figure 7: Sample during titration at the end of titration



Figure 8: Sample at the end of titration

The solution in the flask was titrated with solution in the burette in boiling conditions until disappearance of blue color and the volume at which brick red color observed were recorded (Figures7&8). For each sample the sugar content was calculated by method suggested [15] the outputs of the experiment were fed in to design expert software and process optimization was done accordingly

$$R_s(\%) = \frac{300\text{ml} * f}{V} * 100 \dots \dots \dots (7)$$

Where: Rs (%) is percentage reducing sugar, f = 0.051 (Fehling factor), V is volume used in the titration (titrate value) (mL) and mL is milliliter.

Batch Fermentation Studies

Batch fermentations were carried out in Erlenmeyer flasks with 1000 ml of production medium. The medium was distributed equally in six sterile flasks, each containing various initial concentrations of substrate. 2% (v/v) of inoculum medium was transferred to each 600 ml production medium in sterile conditions. Samples were taken from the solution at regular time intervals (day1, day2 and day3) for the analysis of alcohol by volume concentration. Ethanol concentration in the fermented broth was estimated taking specific gravities of the samples and correlating it with alcohol by volume concentration.



Figure 9: Sample of Inoculums



Figure 10: Saccharomyces Cerevisiae



Figure 11: Fermentation flasks in a water bath



Figure 12: Fermented Broth Sample

Distillation Process

The fermented mixture was heated using a heater and distilled via simple distillation and different batches of distillation (re-distillation) were conducted to increase the concentration of the samples where samples having high concentration of ethanol were chosen for property tests.



Figure 13: Fermented Broth Distillation



Figure 14: Re-Distillation of Sample

Determination of the Properties of Ethanol

Appearance: The distillate was observed visually, using visual test method. The pH refractive index and specific gravity of the distillate was determined by employing the same methods used in the determination of fermented broth properties.

Ethanol Yield

Ethanol concentrations were monitored by taking reading of alcoholmeter and by calculating the volumetric.



Figure 15: Alcoholic Content Measurement

PH Test

The same procedure used previously (7.4.1) was used in this test where the sample changed to ethanol instead.

Density and Specific Gravity Test

Empty graduated cylinder was filled with the sample (Ethanol) and the specific gravity of the sample was measured with hydrometer and the density of the sample was calculated using the relationship between density and specific gravity.

Physicochemical Property Tests

pH

The pH was measured using a pH meter which is of the digital type. The pH of the broth undergoing fermentation was measured periodically by dipping the pH meter into the samples and recording the displayed values.

Refractive Index

The refractive indices of samples from fresh and fermented palm wine and hydrous and anhydrous bio-ethanol were measured using the refractometer. The samples were each inserted drop wise onto the refractometer screen which was in turn closed. The value was displayed almost immediately.

Specific Gravity and Alcohol Content

The specific gravities at 20°C of samples from fresh and fermented palm wine and hydrous and anhydrous bio-ethanol were measured using the hydrometer, while the alcohol content by volume of the fresh and fermented broth was measured using equation 8.

$$ABV_{(\%)} = \frac{Sg_1 - Sg_2}{0.789} * 100 \dots \dots \dots (8)$$

Where: ABV, Sg1 and Sg2 are the percentage alcoholic content, initial specific gravity and final specific gravity, respectively.

Viscosity Test

The same procedure for oil and Methyl Ester viscosity measurement was used for this test.

Alcoholic Concentration Measurement

Frequent alcoholometry reading was taken for every sample in question and the percentage of ethanol in the sample can be read from the instrument directly.

Briquette Production

Mixing Process

Prior to briquetting process, slurries collected from the dilute acid hydrolysis were mixed with certain compositions of glycerol to dilute acid residue ratios of (15:85, 25:75, 40:60% by wt) and 50g of water. The glycerol produced from the experiment was not sufficient so that laboratory grade glycerol used instead. The percentage composition of the binder addition and were characterized based on the weight of slurries used for a smooth briquetting process. The glycerol and water were weighed according to the desired percentage of composition. Then, they were mixed mechanically and the mixture was heated for 5–10 minutes until they became sticky. The gluey binder was mixed with the slurries for another few minutes until they are well-mixed. Finally samples were transferred to the briquetting machine (manual briquetting) and briquette samples were characterized accordingly.



Figure 16: Briquette Sample

Briquette Properties

Percentage Moisture Content

The percentage moisture contents were measured by Moisture Analysis. The percentage moisture content was found by oven drying the briquette sample at 105°C until the mass of sample was constant. Then the percentage moisture content of the briquette was calculated by applying the equation herein below:

$$M_c(\%) = \frac{D}{E} * 100 \dots \dots \dots (10)$$

Where: M_c , D, E are percentage moisture content in dry basis, sample weight loss and sample's initial weight.

Determination of Ash Content

The residue left after burning of briquette is known as ash. It is generally composed of inorganic substances. Samples were weighed (A) in a silica basin. Then the basin is kept inside a muffle furnace and the temperature is gradually raised up to 800°C. At 800°C the temperature is kept constant and the incineration of samples was completed by heating the samples for an hour at that temperature. After incineration, the basin was allowed to cool and transferred to a desiccators. After sometime the basin is re-weighed (w_1). Deduction

of w_i (weight of the basin) from w_1 (weight of the basin + ash) gives weight of ash(C) the amount of ash in the sample. Ash content is expressed in per cent of sample (P_{AC}).

$$P_{AC} = \frac{C}{A} * 100 \dots \dots \dots (10.1)$$

Determination of Volatile Matter

The volatile matter, sometimes called volatiles consists mainly of the gases and water and tarry vapours evolved from the sample when it is heated at high temperature. To determine it, samples of briquette were taken in a silica crucible with porous silica cover. The weight of the silica crucible and sample was (A). The cover is used to avoid oxidation. The sample was then heated for 7 minutes at a constant temperature of 925°C inside a furnace. After heating the crucible is cooled and transferred to a desiccator. After few minutes the silica crucible is re-weighed (B). The difference between A and B gives the amount of apparent volatile matter in the sample and the percentage of volatile matter in the sample (P_{VM}) was calculated as follows:

$$P_{VM} = \frac{A - B}{A} * 100 \dots \dots \dots (10.2)$$

Calculation of Fixed Carbon (FC)

The fixed carbon represents the carbon content in a coal that has not combined with any other element (in a free state). The amount of fixed carbon was computed by subtracting the sum of the percentage of moisture, volatile matter and ash from hundred.

$$F_C = 100 - (P_{AC} + M_c + P_{VM}) \dots \dots \dots (10.3)$$

Calorific Values

In this experiment, the energy of a briquette will be determined using a simplified set-up (with 70% efficiency). The sample was burned in air on stove, instead of pure oxygen. Instead of a heavy metal bomb, a metal can, such as an aluminum soft drink can was used. To eliminate the determination of the specific heat of the metal can (the heated needed to heat the metal that composes the can), the experimental conditions are modified to maintain a constant temperature of the can by filling it with a large quantity of ice. This maintains a temperature of 0°C, as long as all the ice does not melt. The heat evolved by the burning sample melt some of the ice and the amount of liquid water formed will be measured to give the heat of combustion of the sample.

The heat produced by the burning sample and a one gram sample of the briquette was calculated by the equation:

$$q_{\text{sample}} = m_{\text{water}} * 80 \left(\frac{\text{cal}}{\text{g}} \right) \dots \dots \dots (11)$$

$$q = \frac{q_{\text{sample}}}{m_{\text{sample}}} \dots \dots \dots (11.1)$$

Where: q , q_{sample} , m_{water} , m_{sample} are heat generated per gram of sample in calories, heat produced by the burning sample in calories, mass of the water in g (this is equal to the volume of the melted ice in ml) and mass of the sample that burned in grams, respectively.

Experimental Design and Statistical Analysis

The experimental data obtained were analyzed for regression and graphical analysis by the software (Design-Expert 10.0.6, StatEase,

Inc., USA). The statistical analysis of the different order model equations were performed in the form of the variance (ANOVA). This analysis includes the Fischer's F-test, correlation coefficient (R), determination coefficient (R²), which measures the proportion of variance explained by the results obtained. The matrix for variables was varied at five levels (-a, -1, 0, +1, and +a). As usual, the experiments were performed in random order to avoid systematic error. The results were statistically processed by analysis of variance at the significance level of α . The adequacy of the model was then evaluated by coefficient of determination (R²) and model p-value. Response surface methodology is a useful model for studying the effect of several factors influencing the responses by varying them simultaneously and carrying out limited number of experiments. The regression analysis was performed to estimate the response function as a selected order polynomial model, then plotting responses as a function of two factors and drawing response surface plots came. For determination of optimal values of examined factors, methods of desired function were applied. Central Composite Design (CCD) it is a design that combines the vertices of the hypercube whose coordinates are given by a factorial design with star points [15]. The star points provide the estimation of curvature of the nonlinear response surface of RSM is then was used for the experimental design to optimize the process parameters and the general equation is given herein below:

$$Y = B_0 + \sum B_i X_i + \sum B_{ij} (X_i X_j) + \sum B_{ii} (X_i)^2 + e \dots \dots \dots (12)$$

Where: Y is the predicted response, B₀ is the value of fitted response at the center point (0, 0, 0), and B_i, B_{ij} and B_{ii} are linear, quadratic and cross product regression terms respectively, and A and B are process variables.

Actual process variables (A&B) are related to the coded process variables are given according to the following equation:

$$X_i = \frac{x_i - x_0}{\Delta X} \dots \dots \dots (12.1)$$

Where x_i / X_i – coded value of ith variable, X_i – un-coded value of the ith test variable, ΔX – difference between the preceding values and X_0 – un-coded value of the ith test variable at the center point.

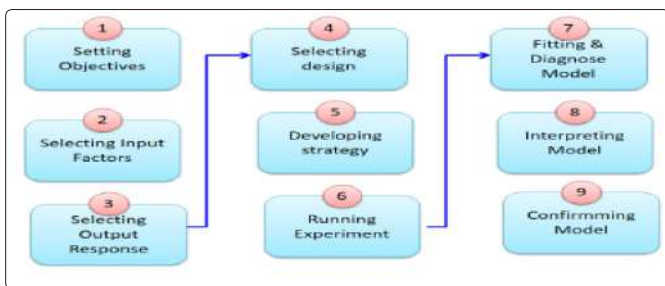


Figure 17: Flow sheet for Statistical Design of experiment

According to the half fraction of CCD, the total number of experiments is $2^q + 2_q + k$, where q is the number of independent variables and k is the number of repetitions of the experiments at the center point.

Trans- esterification

The experimental design employed in this work was a central composite design (CCD) a two-factor five- level. Process variables

Methanol/oil ratio was set at a constant value of 3:1 v/v and A, reaction temperature, and B, reaction time were selected as independent factors for the optimization study. The response chosen was the methyl ester yields obtained from transesterification of refined oil. The matrix for the two variables were varied at five levels (-a, -1, 0, +1, and +a). As usual, the experiments were performed in random order to avoid systematic error. The regression analysis was performed to estimate the response function as a different order polynomial and the best model which is suggested according to model fit test is used to optimize the process. From the general equation Y_i is the Methyl Esteryield.

Table 3.0: Independent variables and levels used RSM design for Trans-esterification

Independent Variables	Symbols	Range and Levels				
		-a	-1	0	+1	+a
Temperature(°C)	A	46.9	50	57.5	65	68.1
Reaction time (min)	B	11.7	20	40	60	68.3

Dilute Acid Hydrolysis

A two variable central composite design (CCD) for response surface methodology was used to develop a statistical model for the hydrolysis process. The range of the variables that were optimized is shown in Table 4:

Table 4.0: Independent variables and levels used for RSM design for dilute-acid hydrolysis.

Independent Variables	Symbols	Range and Levels				
		-a	-1	0	+1	+a
Temperature(°C)	A	79.6	90	115	140	150.3
Acid Concentration (M)	B	0.58	1	2	3	3.4

Result and Discussion

Moisture Content of SCG

The average particle size of dried spent coffee was 1.5mm and the dried SCG sample had 10.2% moisture content.

Oil extraction and Separation

The oil extraction experiment was conducted at optimum conditions operating temperature of 22.5g/g of hexane to oil ratio and operating time as 30.4min as it is reported by the literature, the variation in oil content at the two extreme points were also checked. To collect sufficient amount of oil for the preceding experiments twenty experimental runs were conducted five soxhlet extraction runs were conducted at a time so that the whole extraction process was completed by operating all the five extractors for four batches after the extraction process the temperature of the heating mantel was set at 80°C and samples are heated for 30min to attain nearly complete removal of hexane then the oil was filtered with filter paper and kept in sealed flasks. The amount of oil, experimental yield of oil production was 11.892 % and properties of the resulting oil are reported in below:

Table 5.0: Basic properties of SCG oil in comparison Jatropha oil

Properties	SCG oil	Jatropha oil
Acid Value (mg KOH/g oil)	5.04	8
Percentage Free Fatty Acid	2.52	4.0
Iodine Value (gI ₂ /100g)	85.25	101

Saponification Number (mg KOH/g oil)	168.3	199.24
Viscosity at 40 °C (mm ² /s)	34.2	35.4

Source: R.K Singh; characterization of jatropha oil for the preparation of methyl-ester

Statistical Analysis for Percentage Trans-esterification and Dilute Hydrolysis Process

Design-Expert 10.0.6 (Stat-Ease, Inc.) software was employed for statistical analysis of experimental data. The DOE led to 13 runs with 8 non center points and 5 center points. The levels were chosen according to the properties of experimental limitations, preliminary experiments and previous experience. The experiments were performed based on the design matrix indicated Table. &. All the experimental runs were carried out randomly to minimize systematic errors. The data obtained from the experiments were analyzed to develop a mathematical model and to conduct optimization as well.

Development of Regression Model for Trans-esterification Experiment

A regression models depicting the yield of Methyl Ester for the trans-esterification experiments were developed. The model was carefully selected based on the highest order polynomials. The additional terms were significant, as well as the models were not aliased based on the sequential model sum of squares. Model fitting parameters describing the reaction conditions were calculated and illustrating the design matrix in terms of actual and coded factors. For the percentage Methyl Esteryield, a quadratic model was developed. Equations given in table 10.0 represent the final empirical equations expressed by using the coded factor. Statistical Analysis Various models including linear, two factor interactions, quadratic and cubic were examined sequentially and the quadratic model was suggested because of its low p value (<0.05).

Table 6.0: ANOVA for model selection

Source	Sum of Squares	df	Mean Square	F value	P-Value Prob>F	Remark
Mean Vs Total	76632.74	1	76632.74			
Linear Vs Mean	38.9	2	19.45	0.91	0.4334	
2FI Vs Linear	0.39	1	0.39	0.016	0.9007	
Quadratic Vs 2FI	199.83	2	99.81	51.75	<0.0001	Suggested
Cubic Vs Quadratic	4.49	2	2.24	1.24	0.3645	Aliased
Residual	9.03	5	1.81			

The value of probable F is less than 0.05 for percentage of methyl-ester yield (y), reflecting the significance of the model. From table 7.0, it is observed that temperature (A), Residence time (B) and their quadratic terms of (A²) and (B²) are significant model terms. Referring to table 7.0 F-value for the interaction term was insignificant but omission causes potential error to the response and it was considered to support the hierarchy. For the percentage of Methyl Esteryield (y), temperature was found to have the greatest effect on these responses by showing the highest F-value of 11.17 when it is compared with the residence time (B). Residence time was significant to the responses, but not as noteworthy compared to temperature. The interaction effect (AB) is less pronounced, whereas the quadratic terms (A²) and (B²) with values of F =98.92 and 14.38, respectively were highly pronounced than the linear terms

relative to the percentage yield of methyl-ester, respectively. The small residual row values shows variation in the response which is still unexplained is low and pure error having sum of square value of 0.038 shows that the amount of difference between replicate runs were insignificant. The model F- value of 24.77 implies the model is significant; there is only a 0.03% chance that an F-value this large could occur due to noise.

Table 7.0: ANOVA for response surface quadratic model

Source	Sum of Squares	df	Mean Square	F- value	P-value Prob>F	
Model	239.12	5	47.82	24.77	0.0003	Significant
A-Temperature	21.51	1	21.51	11.14	0.0125	
B-Residence time	17.39	1	17.39	9.01	0.0199	
AB	0.39	1	0.39	0.20	0.6665	
A ²	188.15	1	188.15	97.44	<0.0001	
B ²	26.81	1	26.81	14.58	0.0074	
Residual	13.52	7	1.93			
Pure error	0.038	4	9.515*10 ⁻³			

Analysis of variance (ANOVA) for the selected quadratic model is summarized in Table 8.0. The accuracy of fitting was evaluated by the R² value. The values for R² and the adjusted R² were 0.9465 and 0.9083, respectively.

Table 8.0: ANOVA model analysis for quadratic model

Std.Dev	Mean		C.V %	Press	-2 log Likelihood
1.39	76.78		1.81	95.90	37.40
R-squared	Adjusted R-squared	Predicted R-square	Adeq precision	BIC	AICc
0.9465	0.9083	0.6204	13.475	52.79	63.40

The coefficient of variance (CV) obtained was 1.81 this value indicates the degree of precision with which the treatments were compared. The relatively low value of CV obtained showed that the treatments were carried out with high precision and reliability. 13.561 was obtained reported that the adequate precision gives. The signal to noise ratio suggested that a value greater than 4 is generally desired. The adequate precision value of value of 13.475 which is greater than the desired value 4 indicates an adequate signal and the model can be used to navigate the design space. The coefficient of determination (R²) was obtained as 0.9465 this indicates that 94.65 percent of the variability in the response could be explained by the statistical model while 4.35 percent could not be explained by the independent variables. The 2 log transformation of the likelihood function and the AICc value are lowest for the selected model while they are compared with other models. Since the ideal value of VIF near to 1.00 it supports the effective fitting of the model to the experimental results. The standard error and the coefficient estimate values listed in the table shows that the variation of the Methyl Esteryield when the single parameter A varied while keeping the other parameter B constant are small enough and the 95%CI low and high value for the interaction AB term is changed from negative to positive value its significance is less while it is compared with other terms.

Table 9.0: ANOVA for coefficient estimate of the quadratic model

Factor	Coefficient estimate	df	Standard Error	95%CI Low	95%CI High	VIF
Intercept	81.19	1	0.62	79.72	82.66	
A-Temperature	-1.64	1	0.49	-2.80	-0.48	1
B-Residence time	1.47	1	0.49	0.31	2.64	1
AB	-0.31	1	0.69	-1.95	1.33	1
A2	-5.20	1	0.53	-6.45	-3.95	1.02
B2	-1.96	1	0.53	-3.21	-0.75	1.02

Table 10.0: Final equation in terms of coded and actual factors for the quadratic model

In terms of coded factors	Yield=81.25-1.64a+1.47b-0.31b-5.20a ² -1.96b ²
In terms of Actual factors	Yield =-227.51427+10.49702A+0.58613B-0.00208333AB-0.092445A ² -0.00490775B ²

The predicted values versus the actual (experimental) values of the Methyl Esteryield are illustrated in Fig. 18, the horizontal (x) and vertical (y) axes show the predicted and experimental values, respectively. In this graph the line (y = x) represents perfect fitness which the nearer experimental points to the line represent less difference with the predicted values. According to this figure, an acceptable agreement can be observed between experimental results and quadratic model predictions. The normal probability plot(19) indicates points follow a straight line (a normal distribution), it is expected that some moderate scatter even the normal data whether the residuals follow a normal distribution, in which case the points will follow a straight line. Formal statistical tests are not used for this diagnostic; visual inspection of the graph is sufficient.

dependent variables were represented by the confined surface in the smallest ellipse in the 3D contour. From the fig it is clear that Methyl Esteryield get increase with the increasing reaction temperature. But at the same time when the reaction temperature increases beyond 60°C the trend also get reversed. During optimization the desirability of achieving the optimization goal which is maximizing the Methyl Esteryield, keeping the independent variables in range has to be satisfied and the desirability check shows that at the optimum condition the value is 1 and it indicates that the optimization process met all the set goals. Along with percentage Methyl Esteryield function the contour plot of the desirability function is shown in fig 20&21.

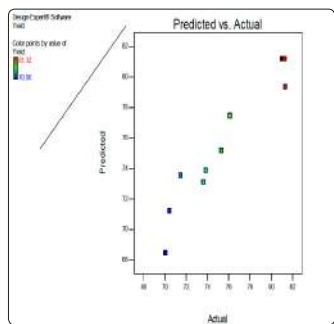


Figure 18: Predicted vs perimental Values

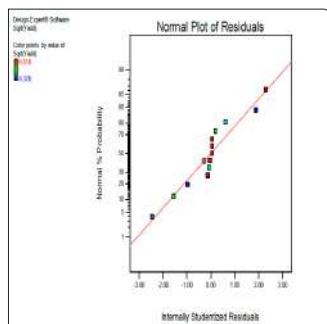


Figure 19: Data Distribution Plot

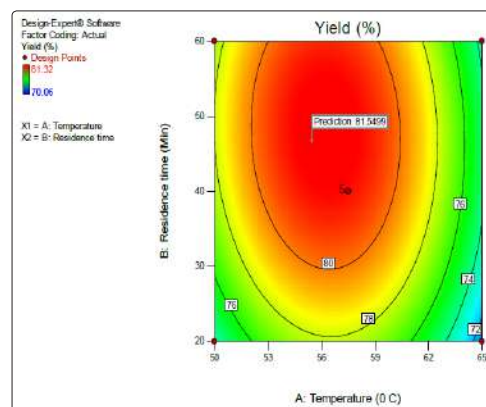


Figure 20: Contour Plot for methylester Yield

Process Variables Optimization

A numerical optimization is also carried out for both responses. Overall optimal conditions are evaluated. The criteria applied for graphical optimization are to maximize the yield of methyl-ester by keeping the reaction variables within the range studied. Under the optimum condition, the corresponding predicted response values of the percentage of Methyl Esterat 57.133°C and 45.117 minute residence time the percentage methyl-ester yield is 81.507 % (9.697%, based on 100g of SCG). The sample was prepared under optimum conditions, 57°C and 45 minute reaction time and the experimental results for the percentage of methylester yield was 79.65% and 20.35% of glycerol was collected this was compared with the predicted values.. The percentage of deviation between the predicted and experimental conditions is small. The contour and 3D response curves were shown below (Figs. 20-22). These curves are showing the effect of independent variables (reaction temperature and time of reaction) on dependent variables (methyl-ester yield). The highest values of Methyl Esteryield with respect to different

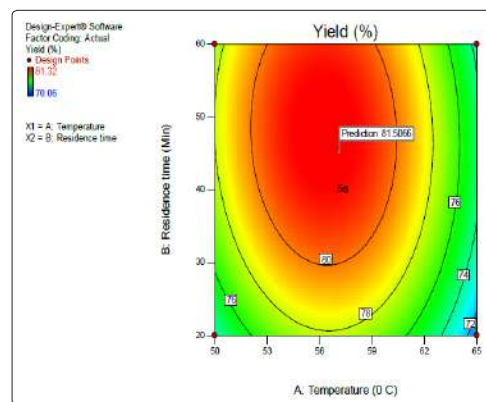


Figure 21: Contour Plot for Desirability Function

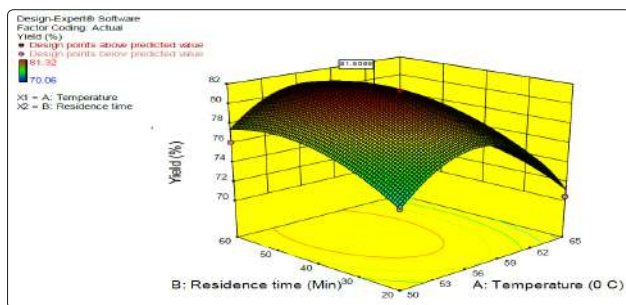


Figure 22: 3D Plot for methyl-ester Yield

This is due to the fact that an increase in temperature above 60°C shifts the reaction temperature towards the boiling point of methanol alcohol this in turn causes the vaporization of methanol and due to the operating pressure for the experiment is atmospheric pressure and no pressure vessel is used in the process the vapor starts to escape from the reaction flask and the reaction rate was started to decrease so that the percentage Methyl Esteryield getting lower and lower. Theoretically, Methyl Esteryield increases with the increase of time due to more time available for reaction but the effect of temperature increment beyond the boiling point of the alcohol (methanol) will hinder the process.

Methyl-ester Properties

Table 11.0: Comparison of methyl-ester with Methyl Esterstandards

Properties	Units	Determined values	Standard	
			ASTM	EN
Iodine value	gI ₂ /100g	76.45	-----	120maximum
Acid value	mg KOH/g	1.02	0.5maximum	0.5maximum
Flash point	°C	450.95	93.0minimum	120 minimum
Saponification number	mg KOH/g	163.25	-----	-----
High heat value(HHV)	MJ/kg	41.59	-----	-----
Cetane Number		62.53	48-65	
Viscosity at 40 °C	mm ² /s	6.4	1.9-6.0	

A slightly higher acid value of 1.02 is not as large as cause polymerization and so that this could not lead to hydrolysis of the methyl-ester. The kinematic viscosity of the resulting methyl-ester which was not far from the standard showed this product can be used for fueling purpose with good distribution and atomization. Due to lower iodine value and viscosity in standard range, the fuel aging problems due to polymerization and oxidation degradation will not be a problem. The cetane number which is in standard range implies relatively short ignition delay and better properties. The higher flash point of Methyl Estershow it is safe for handling and storage point of view.

Development of Regression Model for Dilute Acid Hydrolysis Process

A regression models depicting percentage yield of reducing sugars for the dilute acid hydrolysis experiments were developed. The model was carefully selected based on the highest order polynomials. The additional terms were significant, as well as the models were not aliased based on the sequential model sum of squares [26]. Model fitting parameters describing the reaction conditions were calculated from the data illustrating the design matrix in terms of actual and coded factors (table 16). For the percentage yield of reducing yield, a 2FI model was developed.

Table 12.0: ANOVA results for response surface model

Source	Sum of Squares	df	Mean Square	F value	P-Value Prob>F	Remark
Mean Vs Total	18281.25	1	18281.25			
Linear Vs Mean	7.59	2	3.79	19.39	0.0004	
2FI Vs Linear	0.89	1	0.89	7.56	0.0225	
Quadratic Vs 2FI	0.22	2	0.11	0.92	0.4427	
Cubic Vs Quadratic	0.17	2	0.087	0.65	0.5629	
Residual	0.67	5	0.13			
Total	18290.79	13	1406.8			

The value of probable F is less than 0.05 for percentage of Methyl Esteryield (y), reflecting the significance of linear model. From table 13, it is observed that temperature (A), Residence time (B) and their interaction term of (AB) are significant model terms. For the yield of reducing sugars (y), temperature was found to have the greatest effect on these responses by showing the highest F-value of 19.07, temperature was significant to the responses with an F-value of 45.14, but not as noteworthy compared to acid concentration. The interaction term (AB) has moderate effect on the model. The small residual row values shows variation in the response which is still unexplained is low and pure error shows that the amount of difference between replicate runs was insignificant. The coefficient of determination (R²) was obtained as 0.88886 this indicates that 88.886 percent of the variability in the response could be explained by the statistical model while 11.114 percent could not be explained by the independent variables. The 2 log transformation of the likelihood function and the AICc value are lowest for the selected model while they are compared with other models.

Table 13.0: ANOVA results for selected 2FI

Source	Sum of Squares	df	Mean Square	F- value	P-value Prob>F	
Model	8.48	3	2.83	23.92	<0.0001	Significant
A-Temperature	2.25	1	2.25	19.07	0.0018	
B-Acid Concentration	5.33	1	5.33	45.14	<0.0001	
AB	0.89	1	0.89	7.56	0.0225	
Residual	1.86	9	0.12			
Lack of fit	0.92	5	0.18	5.10	0.0699	Not significant
Pure Error	0.14	4	0.036			

Table 14.0: ANOVA model analysis for 2FI

Std.Dev	Mean		C.V %	Press	-2 log Likelihood
0.34	37.5		0.92	3.84	4.35
R-squared	Adjusted R-squared	Predicted R-square	Adeq precision	BIC	AICc
0.88886	0.8514	0.5978	15.599	14.61	17.35

The coefficient of variance (CV) obtained was 0.92 this value indicates the degree of precision with which the treatments were compared. The relatively low value of CV obtained showed that the treatments were carried out with high precision and reliability. An adequate precision value of 15.599 was obtained reported that the

adequate precision gives the signal to noise ratio which is suggested that a value greater than 4 is generally desired. The value of 15.599 obtained indicates an adequate signal and the model can be used to navigate the design space. The coefficient of determination (R^2) was obtained as 0.88886 this indicates that 88.886 percent of the variability in the response could be explained by the statistical model while 11.114 percent could not be explained by the independent variables. The 2 log transformation of the likelihood function and the AICcs value are lowest for the selected model while they are compared with other models. Since the ideal value of VIF near to 1.00 it supports the effective fitting of the model to the experimental results. The standard error and the coefficient estimate values listed in the table shows that the variation of the methyl-ester yield when the single parameter A varied while keeping the other parameter B constant are small enough and the 95%CI low and high value for the interaction AB term is changed from negative to positive value its significance is less while it is compared with other terms.

Table 15.0: ANOVA for RSM quadratic model for coefficient estimates

Factor	Coefficient estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	37.50	1	0.095	37.28	37.72	
A-Temperature	0.53	1	0.12	0.2	0.81	1
B-Acid Concentration	0.82	1	0.12	0.54	1.09	1
AB	0.47	1	0.17	0.084	0.86	1

Table 16.0: Final equations in terms of coded and actual factors

In terms of actual factors	Reducing sugar=38.21458-0.027620A-1.86095B+0.0315AB
In terms of coded factors	Reducing sugar=37.50+0.53a+0.82b+0.47ab

The predicted values versus the actual (experimental) values of the Methyl Esteryield and distribution plots are illustrated in Fig. 23&24. The horizontal (y) and vertical (x) axes show the predicted and experimental values, respectively. In this graph the line ($y = x$) represents perfect fitness which the nearer experimental points to the line represent less difference with the predicted values. According to this figure, an acceptable agreement can be observed between experimental results and quadratic model prediction

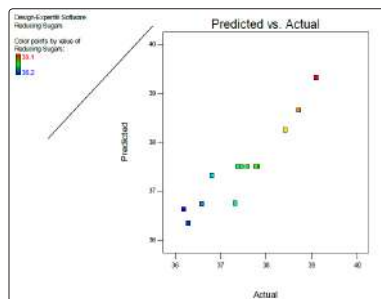


Figure 23: Predicted vs Actual Values

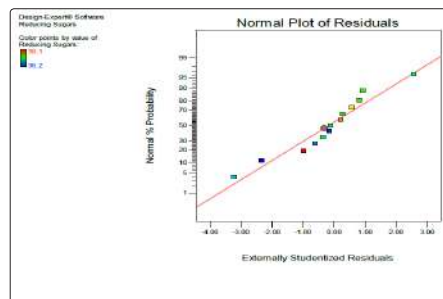


Figure 24: Plot for Data Distribution

Process Variables Optimization

A numerical optimization for reducing sugar yield was evaluated by setting criteria for graphical and numerical optimization were maximization of the yield of reducing sugars while keeping the temperature and acid concentration in study ranges. Under the optimum condition, the corresponding predicted independent variable values of operating parameters are of 98.605°C temperature and of 2.967M acid concentration the 39.1605 percent of reducing sugars yield was achieved. The confirmation run under optimum conditions was conducted to check the precision of the model and 37.28 percent was attained, comparing this value with the predicted ones the deviation is small. The contour and 3D response curves were shown below (Figs. 25&26). The effect of independent variables on reducing sugars yield is clearly represented on the curves with the highest values of the reducing sugar yield were represented by the confined surface in the smallest ellipse in the 3D contour surface in the smallest ellipse in the 3D contour. The maximum desirability of 1 was also achieved. From the figure it is clear that reducing sugar yield get increase with the increasing temperature at the optimum acid concentration the operating temperature will approach to the boiling point of the water so that the water starts to vaporize rapidly which in turn causes a sample with a high concentration of acid which is not good for the fermentation process and it may require another operation to reduce the acidity of the sample which is cost and labor intensive.

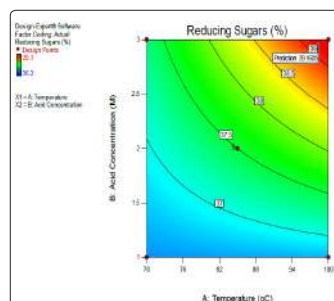


Figure 26: Contour Plot for Desirability

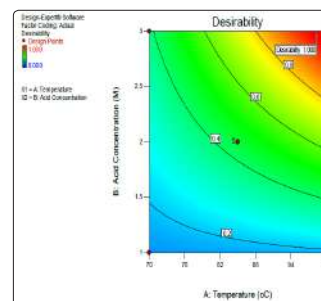


Figure 26: 3D Plot for Reducing Sugar Yield

Batch Fermentation Experiment

The pH of the sample from dilute acid hydrolysis experiment was adjusted with 1M of NaOH solution and the adjustment was continued until a slightly acidic solution was attained. The fermentation experiment was held for four days and the representative samples were taken out on each day and the pH, specific gravity and based on the specific gravity alcohol by volume concentration were calculated and recorded.

Table 17.0: Batch fermentation experimental results

Properties	Initial	Day1	Day2	Day 3	Day 4
pH	6.6	6.4	6.2	5	4.01
Specific gravity	1.98	1.97	1.95	1.89	1.83
Alcohol Content(ABV)	0	1.267	2.534	7.6045	7.6045

The efficiency of the fermentation experiment was determined from the stoichiometric yield. From the literature given above in the introduction the monosaccharide in spent coffee ground are basically 60 percent glucose and 40 percent of mannose from the experiment at optimum condition 37.28 percent of reducing sugar was found per 300ml of sample. This indicates that 111.84 ml of the sample was reducing sugar, using the density of glucose (1.54g/ml), it is found that there is 172.233 g. Considering, 60 percent of glucose 103.34g and taking 300ml sample from stoichiometry 0.511g of ethanol /g of glucose so that 52.80g of ethanol is formed and using the density of ethanol (0.7893g/ml) the volume of ethanol is 66.89 ml from the experimental result of 7.6045 %v/v there is 22.8135 ml in 300ml of sample volume based on stoichiometric yield the percentage of glucose to ethanol conversion is 34.1percent.

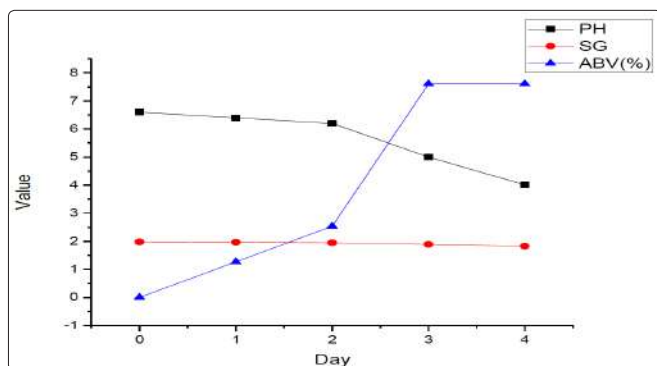


Figure 28: Plot for Batch Fermentation Results

From figure 28, the decrease in the specific gravity value is slight but the value of the resulting alcoholic by volume percentage concentration is increased. Initially, an increase of ABV value is sluggish this is due to the adaptability of the yeasts to experimental environment. Once the yeasts adapt the environment the fermentation reaction rate gets higher and higher until it reaches day 3 and pH 5 at this point the maximum ABV value was achieved which is 7.6045 at the fermentation day reaches at day 4 there were no change in the value of ABV. This is due to a sharp increase in acidity which creates unfavorable condition for the yeasts.

Simple Batch Distillation Experiments

Three different batches of simple distillation experiments were conducted at fixed residence time of 2 ½ hrs and the operating temperatures were decreased from batch to batch this is due to an

increase in the value of ABV which causes a decrease in the boiling point the range of temperatures were selected from the relationships of ethanol concentration and boiling point curves. The ABV values were determined by the alcoholmeter and calculations for efficiencies based on ABV concentration and volumetric yield were calculated. The ethanol recovered had 1.36 RI and 7.46pH value with a colorless appearance. The following table 18.0 shows the results for three batch simple distillation. ABV was increased from batch to batch but the efficiencies of the process got lower and lower this is due to the decrease in sample volume while the sample reaches at their equilibrium faster and faster so that the separation process was difficult from batch to batch the maximum ABV value achieved by the experiment was 55%.

Table 18.0: Batch distillation experimental results

Operating time (hrs)	Temperature (°C)	Sample size (ml)	Initial ABV (%)	Volumetric yield (ml)	Final ABV (%)
2 1/2	85	600	7.6045	196	35.3
2 1/2	82	400	35.3	184	47
2 1/2	79	213	47	187	55

Briquette Formation Experiment

The briquette formation experiment was conducted at a chosen glycerol to briquette ratios of 15:85, 25: 75, 40:60, the glycerol found from this research was not sufficient for the experiment so a standard laboratory grade liquid glycerol was used instead, and the resulting sample was tested for ash, volatile matter contents, fixed carbon content and the calorific values were determined according to the equations 11 and 11.1, respectively.

Table 19.0: Proximate analysis and calorific value results for briquette production

Glycerol to briquette ratio (wt %)	A (%)	VM (%)	FC(%)	MC(%)	HHV(MJ/kg)
15:85	4.04	86.83	1.9	7.23	13.35
25:75	3.95	88.15	1.74	6.16	13.99
40:60	3.86	88.80	1.72	6.12	13.58

From Table 19, the study found that in the range of 15:85, 25:75, 40:60 glycerol to spent coffee ground residue ash content of samples were in a range 3.5-5%, except the 40:60 ratio sample thrash content of other samples were slightly greater than that of firewood (3.9%), but for all samples the ash contents were less than that of wood charcoal's (5.4%). The volatile matters of the sample were in the range of 85-88%, increasing with increment of glycerol addition this was due to the vaporization of glycerol which contributed to the increment of volatile matter. Fixed carbon contents of the samples were in a range 1-2% which was lower than that of the firewood's 22.8% and very much lower than wood charcoals 84.6%. At highest ratio of SCG to glycerol, there was slightly highest value of fixed carbon content, this was due fixed carbon was basically related with the SCG residue and the higher the amount in SCG residue, the higher its fixed carbon content. A decrease of calorific value (HHV) of the samples while increasing glycerol to SCG residue was due to an increase in volatile matter which increased a potential heat skipping with it while the variation of the moisture content in the moisture content values was not greater than 1.5% and the decrease in the moisture content of the sample was due to more and more

of the moisture was retained in the SCG residue and as the ratio of SCG to glycerol increased the retained moisture was escaped due to the heating process so that the moisture content was increased slightly but the smallest moisture content was not decreased below 6.12% this was due to the bonded moisture in the SCG residual and the rate of removing this moisture content is not as fast as the free moisture removal rate so it takes very long time to decrease the moisture content below this value.

Table 20.0: Physical status for briquette samples

Ratio (glycerol:SCG residue)	Status
15:85	Not moldable
25:75	Easily moldable
40:60	Easily moldable

From table 20, at the lowest glycerol to SCG residue ratio of 15:85 the physical status of the sample was malleable; this was due to the less binding tendency of the sample. The higher amount of glycerol, the more the binding efficiency would be so that the sample was hold together easily, however it takes some time to remove from the briquette machine, higher binder (glycerol) addition enabled a molding process to be conducted more easily.

The general mass balance for the sequential production of biodiesel, bioethanol and briquette from SCG was performed by taking 100 g of SCG sample as a basis and the percentage oil extraction, Methyl Ester yield and glucose to bioethanol conversion were taken for the calculations. Moreover, calculations for trans-esterification and dilute acid hydrolysis process was done at the optimum process conditions and the data is presented in Table 21:

Table 21: General mass balance for sequential production of methyl-ester, bioethanol and briquette from SCG

Unit Operations	Inputs (g)	Outputs (g)
Soxhlet Extraction	100 g(SCG)	11.892g (oil)
		88.108g (Raffinate)
Trans-esterification	11.892 g(Oil)	9.47 g (Biodiesel)
		2.44 g(Unconverted oil, glycerol and others.)
Dilute Acid Hydrolysis	88.108 g(Raffinate)	13.136 g(Mannose)
		19.7 g(Glucose)
		43.368 g(Dried Solid Residue)
		11.886 g of moisture
Fermentation	13.136 g(Mannose) 19.7 g(Glucose)	3.43 g (Ethanol)
		13.136 g(Mannose)
		16.27 g (Glucose)
Total	100 g	100.00 g

Conclusion and Recommendations

Conclusion

The percentage of oil extracted from the SCG (11.892%) was reasonably higher to be used for methyl-ester production and the production of methyl-ester and dilute acid hydrolysis experiments were conducted. CCD optimization model was used to represent the experimental values and the precision of the models used for Trans esterification and dilute acid process having the determination

coefficients of 0.9465 and 0.88886, respectively with experimentally validated optimization outputs of 79.65% for Methyl Ester and 37.28 % reducing sugar at optimum parameters of temperature, residence time, and acid concentration. The quality of the obtained methyl-ester was comparable with the ASTM and EN standards. The resulting reducing sugar from the dilute acid hydrolysis process gave a potentially good ABV value of (55%) ethanol and this in turn showed the potential that of concentrating the resulting ethanol to fuel grade passing through reflux fractionating column. Briquettes produced from the SCG residue at 25:75 glycerol to SCG residue having combustion levels; calorific value of 13.35MJ/kg, Volatile matter of 88.15% and 3.95 % of ash content) less than fire woods(19-22MJ/kg)and charcoal (29.6MJ/kg) the lesser in ash content makes it very good option for household fueling so that an integrated fuel outputs of the SCG showed that it can be used as raw material for biofuel production which can contribute a lot in replacing the non-renewable energy sources to renewable once and this in turn can minimize the waste accumulation in towns with successfully change this waste to energy conversion as an income generating sector.

Recommendations

Based on this research it is recommended that:

- Researches shall be conducted on different methods of hydrolysis process other than dilute acid hydrolysis process to enhance the conversion of polysaccharides in to reducing sugars.
- Scientific investigation and genetic modification of yeast strains that can digest other sugar types in SCG shall be done and this may in turn leads to highly efficient conversion of sugars to ethanol.
- The simultaneous saccharification and fermentation process shall also be investigated to check whether it adds efficiency on the alcoholic production process
- Agricultural researches for a modified coffee seeds which will add values both on coffee quality (with high contents of sugar and lipids) which can enhance spent to biofuel conversion potential shall be conducted.
- Research on economic feasibility including logistics of SCG collection and large scale production of biofuels has to be studied based on this and other research outputs.
- Using lab equipment such as UV spectrometer, HPLC, bomb calorimeter and IR should be used for determination of reducing sugar yield, characterization of Methyl Ester properties and calorific values of briquette samples is essential to avoid and minimize possible errors.
- The cloud point, freezing point for oil and Methyl Ester and ultimate analysis for briquette samples which weren't conducted in this study should be done in the future.

Acknowledgment

First and foremost, praises and thanks to the God, the Almighty, for His showers of blessings throughout my research work to complete the research successfully. A special gratitude to my thesis advisors, Prof. Venkata Ramaya and Mr. Gebeyehu Abu, whose contribution in stimulating suggestions and encouragement, helped me to coordinate my work especially in writing this thesis. Furthermore I would also like to acknowledge with much appreciation the crucial role of the staff of Debre Birhan Agricultural Research Center (DARC), who gave the permission to use all required equipment and the necessary materials to complete the task. A special thanks goes to Mr. Ashenafi Kebede, assistant laboratory researcher for animal

nutrition department at DARC, who help me a lot in giving assistant for using laboratory instruments there. Last but not least, many thanks go to the head of the School of Chemical Engineering at JiT who was highly supportive in letting me use the laboratory facilities of the school and I also appreciate the co-operation of Jimma University College of Agriculture and Veterinary Medicine, Department Post Harvesting Management for letting me use some of their laboratory facilities.

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