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Upgrading and Optimization of Pyrolysis Oil from Corncob (*Euphorbia mammillaris*) and Peanut (*Arachis hypogaea*) Shells by Liquid-Liquid Extraction Process

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Abstract: *The bio-oils from peanut shells and corncobs have limited applications due to high oxygen content, viscosity, acidity, and organic compounds, necessitating upgrading. This study employed liquid-liquid extraction to improve oil quality due to its affordability. Bio-oils were produced via intermediate pyrolysis in a fixed-bed reactor at 450 °C, followed by physicochemical and GC-MS analysis. The need for further treatment led to the use of a low-cost, simple liquid-liquid extraction method. A Box-Behnken experimental design was applied, considering temperature, time, and solvent as parameters. Extraction temperatures of 25 °C, 40 °C, and 55 °C were tested alongside extraction times of 30, 60, and 90 minutes using n-hexane and ethanol as solvents in a 1:2 ratio with bio-oil. N-hexane achieved higher phenolic compound extraction efficiency, yielding 68.21% for corncob bio-oil and 66.94% for peanut shell bio-oil, compared to 60.95% and 58.87% using ethanol at 55 °C. The process also improved pH values from 4.7 to 5.7 for peanut oil and from 4.5 to 5.8 for corncob oil, reducing acidity and operational costs. It was concluded that higher extraction temperatures increased bio-oil yield up to a critical limit, while n-hexane proved more effective than ethanol in enhancing oil quality and reducing acidity, thereby solving transportation and storage challenges.*

Keywords: Biomass, pyrolysis, extraction, bio-oil, physicochemical analysis.

1. INTRODUCTION

The world population is growing astronomically with respect to the high demand for energy resources [1, 2]. The major energy demand includes coal, petroleum, and natural gas [3, 4] which remain inadequate for today's world energy needs [5]. Given concern about future energy shortages and increasing environmental challenges, intensified research is underway in finding suitable and cost-effective alternatives [6] in relation to renewable energy sources like biomass which account for 9% consumption of the total global energy [7]. Biomass energy is safe and eco-friendly [8].

Pyrolysis oil popularly known as bio-oil is a second-era fluid fuel and a product of thermo-chemical conversion of biomass in the absence of oxygen [9, 10]. This process yields 75% liquid, 10-20% char, and non-condensable gases (10-20%wt of biomass) [11] with many proposed applications which include fuel in boiler systems, gas turbines, and as a treatment step in the conversion of biomass to higher energy content [12]. This application is limited due to high oxygen-rich constituents such as aldehydes, ketones, acids, and water [13] which makes pyrolysis oil have low oxidation stability, high viscosity, low heating rate, and corrosiveness [14]. These properties make pyrolysis oil impossible to use directly as a transportation fuel [15]. The removal of oxygen and other constituents in pyrolysis oil which is of great disadvantage to its usage is referred to as upgrading [16, 17].

Upgrading of pyrolysis oil can be achieved either via physical method or chemical method [18]. The physical method includes filtration, liquid-liquid extraction, emulsification, distillation, and chemical processes include fluid catalytic cracking, hydrogenation, steam reforming, catalytic esterification, and co-pyrolysis method. The chemical method is more expensive than the physical methods concerning the cost of operation and setup. However, liquid-liquid extraction is cost-effective [19, 20].

Liquid-liquid extraction separates bio-oil into different chemical groups thus reducing the rate of viscosity, oxygen content, and aromatics compound which enhances corrosion leading to an increase in operating cost and damage to equipment [21, 22]. This present study seeks to improve the quality of pyrolysis oil produced from corncob and peanut shells using n-hexane and ethanol as solvents in the liquid-liquid extraction process. A statistical approach, the response surface methodology (RSM), is employed in the process optimization of the operating parameters. RSM helps to evaluate multiple factors, and their interactions, and reduce the number of experimental runs required to help achieve a faster and more authentic experimental process [23]. The Box-Behnken design (BBD) is one of the many types of designs available at RSM which has been widely used to optimize biodiesel production [24]. This is because is more effective in parameter optimization, and process prediction [23, 25].

Corncob was chosen as a feedstock due to its high cellulose content, abundant availability, low ash content and renewable and sustainable properties. Peanut shell choice is due to its low sulphur content, richness in lignin and its agricultural waste utilization properties. Both feedstocks exhibit carbon neutrality and improved energy security. The novelty of the research is that the biomass used for the production of bio-oil is from a renewable energy source which offers a sustainable alternative to fossil fuel. It stimulates waste valorisation in which value-added products are created and waste disposal issues are reduced. Scalability and cost-effectiveness remain germane for the integration of existing infrastructure through blending with conventional oil. Diversification of feedstock is enhanced through the research and life cycle assessment enabling the evaluation of the environmental impact and benefit of the oil upgrade process [26].

2. MATERIALS AND METHODS

The biomass feedstocks (peanut shell and corncob) used for this research are shown in Figure 1. They were collected from the Arada and Odo-Oba markets in Ogbomoso, Oyo State Nigeria (8.116° N 4.24° E). The samples were separated from dirt and thereafter, crushed using mortar and pestle for size reduction before grinding into fine particles using a grinding machine.

2.1 Production of Bio-Oil from Corncob and Peanut Shell

To produce oil from corncob and peanut shells, intermediate pyrolysis was carried out using a batch reactor as shown in Figure 2. The reactor was loaded with the feed and brought up to a temperature range of 450 °C with electrical energy as the heating source. An inert environment was created by feeding nitrogen gas into the reactor as seen in Figure 2. After leaving the reactor, the bio-oil was in gaseous form as a result of the high temperature in the reactor and then converted into liquid oil upon meeting the condenser filled with ice.

2.2 Process Optimization (Design of Experiment)

This study was centered on the use of Box-Behnken design in RSM via Design Expert 10 software to study the influence of extraction time, temperature, and oil-solvent ratio for extracting the bio-oil from corn cob and peanut shell. Table 1 indicates low and high levels of independent variables for the design.

2.3 Characterization of the Pyrolysis Oil

The final products of extraction were characterized and analysed with respect to the extent of phenolic compound extractions.

Figure 1: (a) corncob (b) size reduced corncob (c) peanut

Figure 2: Intermediate pyrolysis experimental setup

Table 1: Low and high levels of independent variables for the design

Symbol	Variables	Lowest Level (-1)	Highest Level (+1)
A	Temperature (˚C)	25	60
B	Extraction time (Min)	30	90
C	Solvent-oil ratio	0.02	0.04

2.3.1 Density, pH, specific gravity, and heating value

The digital pH meter used was made in Kolkata India with KI-pH-25C as model number. The degree of acidity of the bio-oils was determined in relation to the number of free hydrogen ions. A lab densimeter was used to determine the density of the bio-oil samples (corncob and peanut). The mass and volume of the samples were considered. The densimeter model number is BK-DME300L which was manufactured in China. Each mass of samples was measured using a weighing balance. The heating value (gross calorific value) was determined according to accepted ASTM standards with the use of a bomb calorimeter and the net calorific value was determined analytically using the weight percentage of hydrogen elemental analysis. The model number of the calorimeter used is SABC-7 made in India.

2.3.2 Gas chromatography-mass spectrometry (GC-MS)

The peanut shell and corncob bio-oil were assessed analytically using GC-MS at the Chemical Engineering Laboratory, University of Ilorin to determine the quality and amount of organic, ketones, and aldehyde compounds present in the pyrolysis oil. The bio-oil sample was injected into the device which entered a gas stream that transports the sample into a separation tube known as the capillary column. Helium was used as the carrier gas whereas the various components of the sample are separated inside the column. The GC-MS machine model is a 7890A GC system, 5675C Inert MSD with a triple-axis detector.

3. RESULTS AND DISCUSSION

3.1 Process Optimization Study

The produced corncob oil and peanut oil as shown in Figure 3 were subjected to liquid-liquid extraction for upgrading. The outcome of the experimental runs generated by the software are presented in Tables 2 and 3.

Figure 3: (a) Corncob oil and (b) peanut oil sample produced

3.2 Effects of Extraction Temperature and Extraction Time on the Yield and pH Values

Extraction temperature and time were directly proportional to the yield of the bio-oil. Tables 2 and 3 show that an increase in temperature results in an increase in the yield of the bio-oil and vice-versa. Table 3 depicts the variation of temperature and time as a function of oil yield and pH. The highest yield of corncob and peanut shell bio-oils using ethanol as solvent was 60.95% and 66.94% at 90 minutes and 55 ºC respectively.

Table 2: Input and output variables for upgrading corncob oil using ethanol as solvent

Std	Run	Temp (ºC)	Time (min)	Solvent-Oil ratio	pH	Oil Yield (%)
13	1	40	60	0.03	4.9	47.25
14	2	40	60	0.03	5.4	46.89
16	3	40	60	0.03	5.1	47.18
15	4	40	60	0.03	5.3	48.67
12	5	40	90	0.04	5.6	55.03
8	6	55	60	0.04	5.5	58.36
5	7	25	60	0.02	4.1	10.47
4	8	55	90	0.03	5.6	60.95
1	9	25	30	0.03	3.8	17.33
3	10	25	90	0.03	4.2	33.14
9	11	40	30	0.02	4.5	41.30
10	12	40	90	0.02	4.1	49.11
11	13	40	30	0.04	5.3	46.20
17	14	40	60	0.03	4.9	50.48
6	15	55	60	0.02	5.6	57.65
2	16	55	30	0.03	5.2	54.09
7	17	25	60	0.04	3.9	26.85

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Table 3: Experimental design of upgrading corncob oil using n-hexane as solvent

Std	Run	Temp (ºC)	Time (min)	Solvent-Oil ratio	pH	Oil Yield (%)
8	1	55	60	0.04	5.6	63.10
1	2	25	30	0.03	3.7	20.95
12	3	40	90	0.04	5.4	56.09
5	4	25	60	0.02	4.2	12.11
4	5	55	90	0.03	5.8	68.21
14	6	40	60	0.03	5.3	53.44
10	7	40	90	0.02	5.4	50.61
6	8	55	60	0.02	5.5	61.94
3	9	25	90	0.03	4.3	42.83
9	10	40	30	0.02	4.6	44.28
17	11	40	60	0.03	5.4	54.49
11	12	40	30	0.04	5	47.89
7	13	25	60	0.04	4.3	29.36
16	14	40	60	0.03	5.2	53.05
13	15	40	60	0.03	5.3	52.94
2	16	55	30	0.03	5.4	57.16
15	17	40	60	0.03	5.2	51.39

At a temperature higher than the boiling point of the solvent, there is a decrease in the yield of the bio-oil which supports the research of Afolabi *et al*. [27] that the characteristics of the solvent are significant to higher temperatures in the extraction of phenolic compound from bio-oil. The result of his studies shows that at 64.5 ºC, the yield of the bio-oil becomes small. Also, the 3D surface plot in Figure 4 shows the relationship between extraction time and the yield of the oil. The highest yield of corncob oil of 68.21% was observed at 90 minutes at an extraction temperature of 55 ºC. The pH of the oil was improved as shown in Figure 4 (b) with ethanol as solvent. An extraction time of 90 minutes influences the pH value of peanut oil from 4.3 to 5.8. Tables 2 and 3 show the effect of pH and the process parameters of time and temperature played a significant role as increased temperature lowers the acidity of the oil.

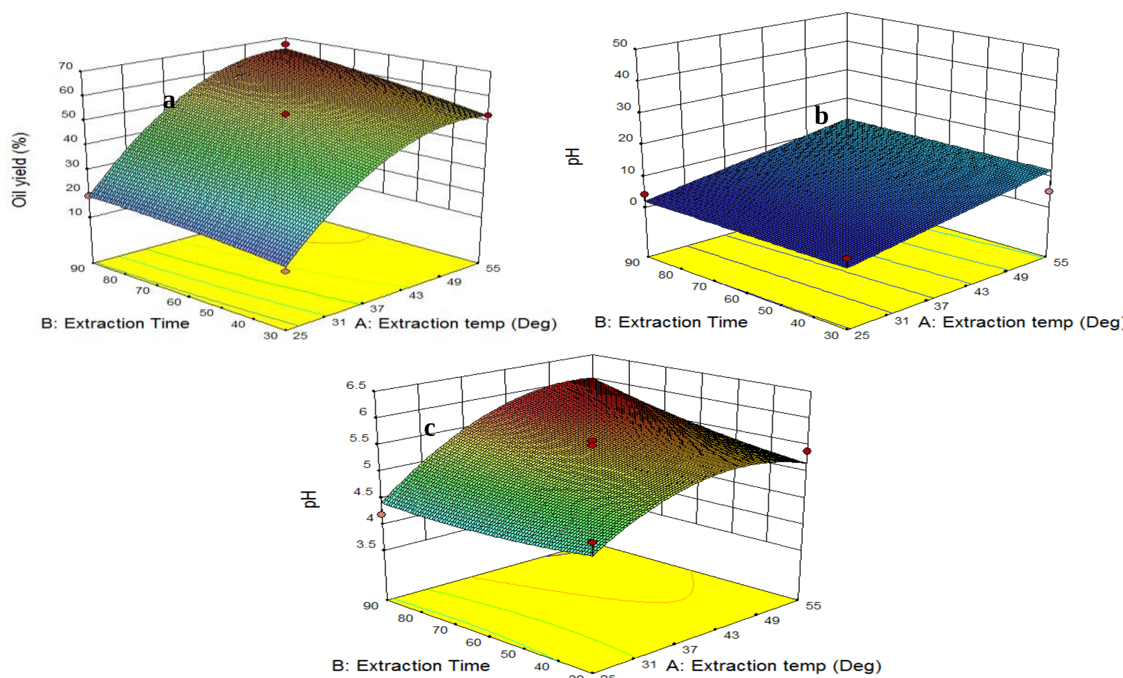

Figure 4: 3D plot of (a) corncob oil yield using n-hexane as a solvent against extraction temperature and time (b) peanut shell oil pH using ethanol as a solvent against extraction temperature and extraction time (c) peanut shell oil pH using ethanol as a solvent against extraction temperature and extraction time

3.3 Effect of Solvent-Oil Ratio and Temperature on the Yield and pH Values

The solvents used were ethanol and n-hexane and the results in Tables 4 and 5 indicate that hexane which is a non-polar solvent has better extraction efficiency with respect to the yield and pH. This is in temperature; solvent dissolution of solute is more efficient leading to higher yield. The higher the temperature, the higher the extraction efficiency which is evident in Figures 5 (a) and 5 (b). At 55 ºC, 90 minutes, and 0.03 solvent-oil ratio, a 60.95% yield of corncob bio-oil was observed and the lowest yield was recorded at 25 ºC and 30 minutes.

Table 4: Experimental design of upgrading peanut shell bio-oil using n-hexane as solvent

Std	Run	Temp (ºC)	Time (min)	Solvent-Oil ratio	pH	Oil Yield (%)
15	1	40	60	0.03	5.6	52.91
17	2	40	60	0.03	5.5	50.73
10	3	40	90	0.02	5.6	49.09
5	4	25	60	0.02	3.9	14.17
9	5	40	30	0.02	4.5	43.79
8	6	55	60	0.04	4.9	54.15
6	7	55	60	0.02	5.5	55.28
7	8	25	60	0.04	4.3	15.46
14	9	40	60	0.03	5.3	49.63
1	10	25	30	0.03	4.8	12.98
11	11	40	30	0.04	5.2	42.91
4	12	55	90	0.03	5.8	66.94
16	13	40	60	0.03	5.5	53.08
12	14	40	90	0.04	5.7	50.81
13	15	40	60	0.03	5.4	51.05
3	16	25	90	0.03	4.2	18.97
2	17	55	30	0.03	5.4	52.37

Table 5: Experimental design of upgrading peanut oil using ethanol as solvent

Std	Run	Temp (ºC)	Time (min)	Solvent-Oil Ratio	pH	Oil Yield (%)
9	1	40	30	0.02	4.4	40.39
11	2	40	30	0.04	4.8	43.97
5	3	25	60	0.02	4.2	13.58
4	4	55	90	0.03	5.6	58.87
6	5	55	60	0.02	3.8	52.29
2	6	55	30	0.03	5.2	49.74
13	7	40	60	0.03	5.4	46.03
8	8	55	60	0.04	45	53.31
16	9	40	60	0.03	4.9	45.64
12	10	40	90	0.04	5.8	48.75
10	11	40	90	0.02	5.7	45.72
15	12	40	60	0.03	5.5	45.9
17	13	40	60	0.03	5.4	45.57
3	14	25	90	0.03	4.3	22.7
1	15	25	30	0.03	4.7	11.3
7	16	25	60	0.04	3.9	15.93
14	17	40	60	0.03	5.3	45.86

The peanut shell bio-oil yield of 66.94% was recorded at the highest temperature of 50 ºC with a sharp decrease in the yield of peanut shell at a solvent-oil ratio of 0.02. The oil acidity improved from 4.2 to 5.8 with the addition of n-hexane which is evident in Figure 5 (c). The boiling point of n-hexane and ethanol were 68 ºC and 78.37 ºC respectively and at temperatures higher than the boiling points of the solvents, oil yield decrease is inevitable. The work of Wijanarko and Putri [28] shows that more phenolic compound was extracted at 60 ºC with a yield of 66.31% and the lowest yield of 11.33% of corncob bio-oil. The acidity of the oil becomes weaker at 5.7 as pH adjustment is achieved which is evident in Table 3, at a higher temperature above 70 ºC, oxygen becomes reduced as the acidic compound is removed, making the bio-oil tending to basic on the pH scale [29, 30].

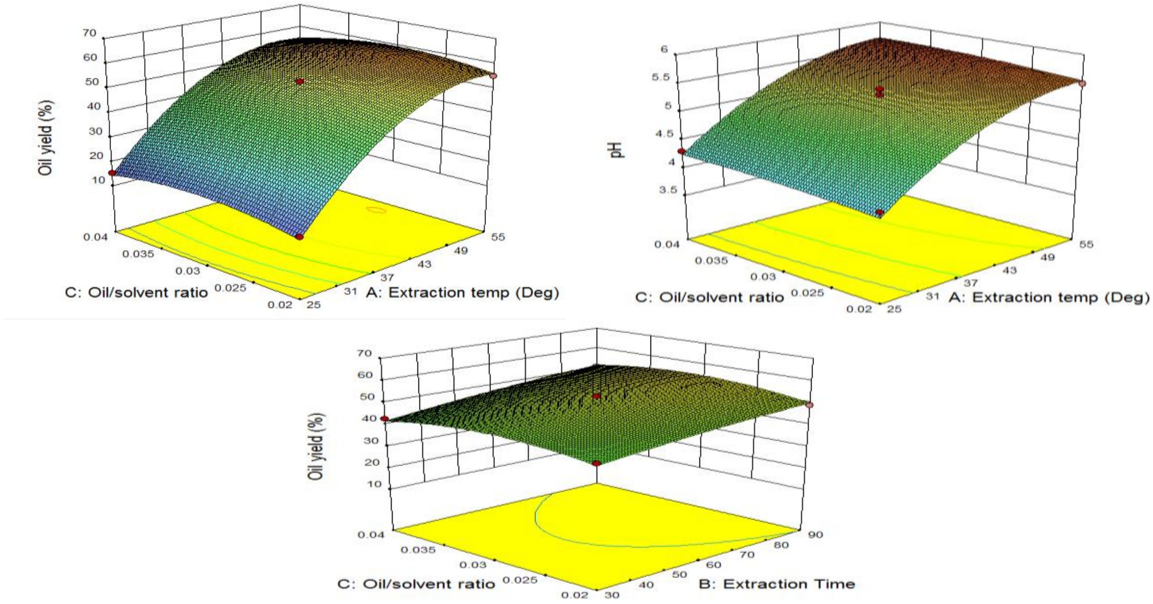

Figure 5: 3D plots using n-hexane against extraction temperature and oil/solvent ratio: (a) peanut shell oil pH (b) peanut shell oil yield (c) corncob oil pH

3.4 Effect of Solvent-Oil Ratio and Extraction Time on the Yield and pH Values

Figures 6 (a) and 6 (b) are the 3D plots of the solvent-oil ratio and time with respect to the yield and pH. Time and solvent ratio favoured the extraction as improvement was obvious in the pH and yield became higher with time. There was an obvious improvement of 3.5-5.7 in the pH of peanut shell oil using n-hexane as a solvent which is evident in Figure 6 (a). The lowest yield of peanut shell and corncob bio-oils was noticed at 30 minutes as shown in Figure 6 (c). The progressive increase in time resulted in a higher yield of the oil and further extension of time above the residence time resulted in a lower yield [31, 32]. Table 5 shows the effect of time on the experimental run. The non-polar solvents have higher extraction efficiency of organics in the bio-oil [33], [34] in which an acceptable level of 66 wt% extraction of phenol was achieved using a ratio 1:1. In Figure 6 (d), n-hexane influences the pH of the peanut shell bio-oil in relation to the extraction time and oil-solvent ratio parameters. At 90 minutes, there was an improvement in the pH of the oil after extraction in which the viscosity of the oil becomes lower as a pH value of 5.7 reduces the acidity and corrosiveness of the oil.

3.5 Characterization of the Upgraded Peanut and Corncob Oil

The bio-oil produced was characterized to determine its quality and composition. The following characteristics of bio-oil such as density, viscosity, pH, and heating value are shown in Table 6. According to Ogunjobi and Lajide [22], the bio-oil produced at 450 ºC is acidic with a pH value of 3.5 and highly viscous which is similar to the result of the physico-chemical analysis of bio-oil produced. The result of the physicochemical properties of upgraded bio-oil shows improvement in the quality of the oil after the extraction process. The moisture content of the corncob and peanut shell bio-oil reduces from 20.3% - 3.4% and 14% - 2.3% respectively which supports the finding of Mohan [31] that a reduction in 85% water content of the bio-oil improves the homogeneity and stability of the oil. The heating rate of the bio-oil derived from peanut shells and corncob after the upgrade in Table 6 enhances the quality of the oil. The viscosity of the corncob and peanut shell bio-oils improved from 0.95-0.38 Cst and 0.87-0.42 Cst respectively which supports the findings of Bridgwater, [35] that high viscous oil can be improved with solvent addition. The higher the heating rate the higher the product yield and thus the heating rate of upgraded bio-oils of both corncob and peanut improved from 16.34 to 35.5 MJ/kg and 17.34 to 31.34 MJ/kg respectively [36].

3.5.1 Gas chromatography-mass spectrometry (GC-MS) analysis

The composition of upgraded bio-oil derived from corncob and peanut shell was analyzed through the GC-MS machine in which a significant reduction in acidic content which is the primary source of corrosion [37] was noticed before and after the upgrade using a liquid-liquid extraction process. Table 6 gives the full composition of the bio-oil before and after the upgrade which enhances the novelty of the research work.

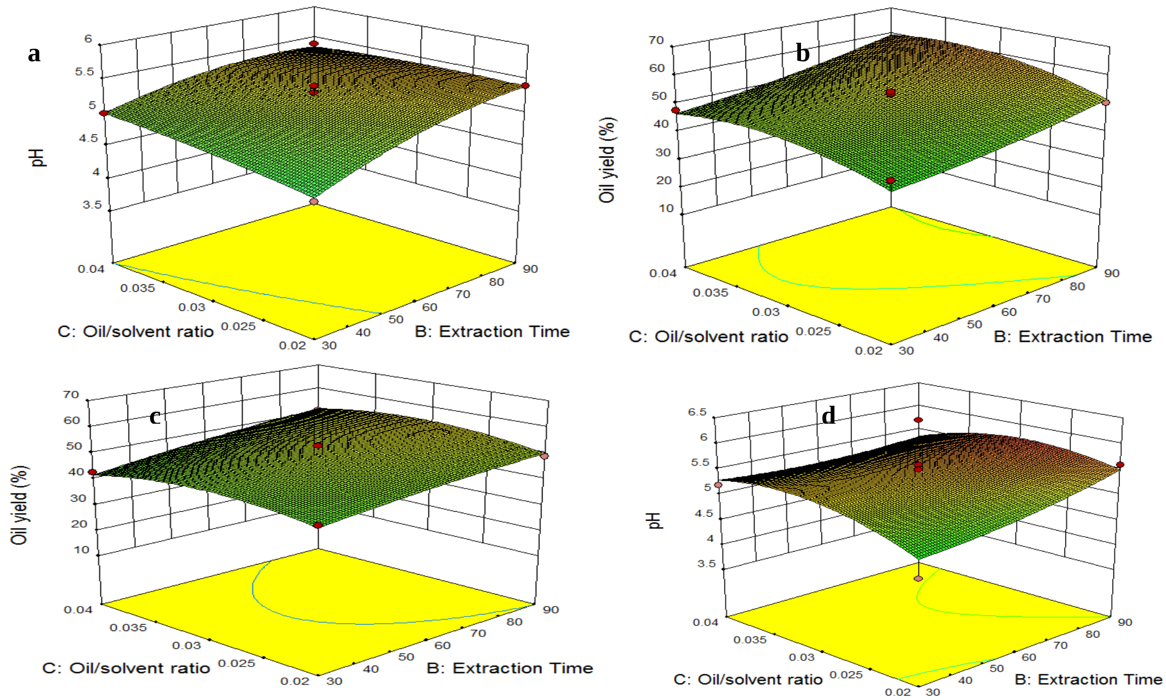

Figure 6: 3D plots using n-hexane against extraction time and oil/solvent ratio; (a) peanut oil pH (b) corncob oil yield (c) peanut oil yield (d) peanut pH

Table 6: Physico-chemical properties of corncob bio-oil

Parameter	Pyrolysis at 450 °C (corncob)	Upgraded Bio-Oil (Corncob)	Pyrolysis at 450 °C (Peanut)	Upgraded Bio-Oil (Peanut)
Density (kg/m^3)	1045	998	1309	1203
Flashpoint (°C)	147	150	336	300
Moisture content (%)	20.3	3.4	14	2.3
Viscosity 40 °C (Cst)	0.95	0.38	0.87	0.42
pH	4.5	5.8	4.7	5.7
Heating rate (MJ/kg)	16.34	35.5	17.34	31.78

The composition of acidic content of upgraded bio-oils of peanut shell and corncob was 11.65% and 7.8% respectively compared to 20% and 11% before the upgrade in relation to Tables 7 and 8. This is in accordance with the research in [38] which there is a pH adjustment with a 40% reduction in the acidic content of the upgraded bio-oil thus reducing the corrosive effect in the process equipment. Figures 6 and 7 reveal both the highest and lowest peaks of chromatograms of upgraded corncob and peanut bio-oil.

Table 7: Composition of corncob bio-oil

Retention Time (min)	Percentage (%)	Composition
2.819	3.05	3-1-buteneMethoxy-2-methyl
5.171	1.98	2-Hexyne, 5-methyl-Acetonitrile, 2-4-dimethyl
6.028	1.56	1,3-Butadiene-1-carboxylic acid, 4-pentynoic acid
6.247	2.30	2-Hexanoic acid, 3,4,4-trimethyl-5-oxo-1-Dimethylamino pyrrole
7.954	2.78	2-Cyclopenten-1-one, 2-methyl-2-Cyclopenten-1-one, 3-methyl-
14.785	6.48	3-Aminoisonicotinic acid Tras-Isoeugenol Phenol, 2-methoxy-3-(2-propenyl1)
18.063	3.37	Hexadecanoic acid, ethyl ester

Retention Time (min)	Percentage (%)	Composition
14.429	3.97	Piperonylamine Phenol, 2,3,5,6-tetramethyl-4-Hydroxy-2-methyl acetophenone
16.89	1.72	1H-Benzimidazole, 2-(1-methyl ethyl ester
17.613	2.64	3-fluoro-1-acenaphthenone
11.539	5.87	Formic acid, phenylmethyl ester silane

Table 8: The composition of peanut shell bio-oil

Retention Time (min)	Percentages (%)	Composition
15.642	4.6	Eugenol, Phenol, 2-methoxy-4-(1-propenyl)-Phenol, 2-methoxy-6-(2-propenyl)
15.99	3.15	Sulfurous acid, butyl dodecyl ester, Dodecane
18.207	1.51	Hexadecanoic acid, methyl ester Pentadecanoic acid, 14-methyl-, methyl ester
14.816	3.49	3-Pyridine carboxylic acid, 2-amino Benzothiazole-2-methanine
13.985	2.27	Phenyl buta-2,3-dienyl ether Quinoxaline, 2-methyl-4,4-oxide
13.797	3.57	Benzene, 1-azido-2-nitro-2,3-Dihydroxystearic acid
13.478	2.31	Tridecane
13.165	3.44	Cyclopropanecarbonyl chloride, 2-phenyl-, trans-Benzocyclobutene, 1-bromo-1-methyl S-Ethyl ethanethioate
8.611	0.49	Phenol, 2,3-dimethyl-Phenol, 2-ethyl-
4.270	3.83	5methyl - 3-Dimethylaminoacrylonitrile1H-Imidazole, 2,4-dimethyl-2-Hexyne
3.419	1.05	3-Pentenal, 4-methyl-3- Hexyn–1–olPhosphonofluridic acid, methyl
11.407	5.98	3-Imididazol – 1 – ylpropanenitrileBenzenemethanol, alpha-ethynyl- 2 Cyclobutene-1- carboxamide
16.693	6.90	Napthalene, 2-(2-nitro-2-2proprnyl) – 3-Trifluoremethylbenzhydryl chloride Florene

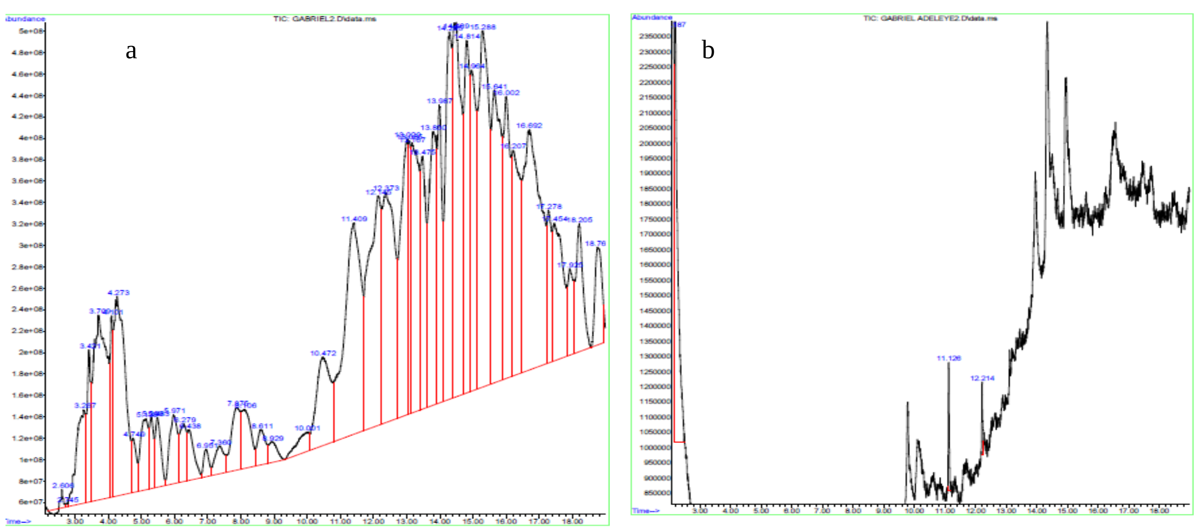

Figure 6: Chromatograph of (a) corn cob (b) upgraded corncob

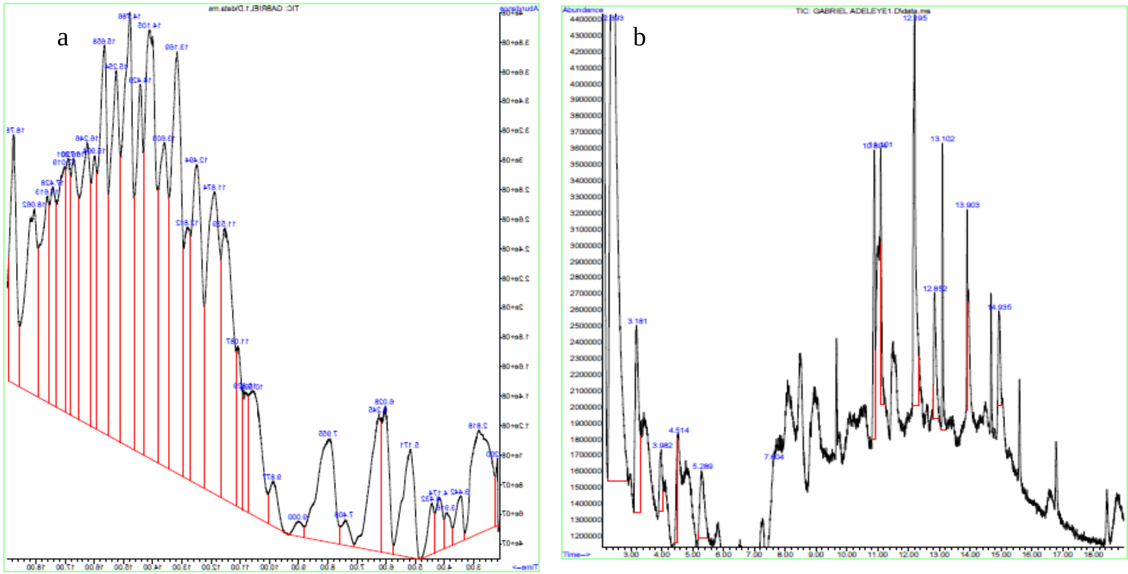

Figure 7: Chromatograph of (a) peanut bio and (b) upgraded peanut bio-oil

4. CONCLUSION

Peanut shell and corncob bio-oils were successfully produced at 450 ºC in a fixed bed reactor via an intermediate pyrolysis. The yield of both oils was determined and the percentage conversion of peanut shell and corncob bio-oil were found to be 68.65% and 76% respectively. The properties of corncob and peanut shell bio-oils were analysed with respect to density, pH, viscosity, heating rate, moisture content, and flash point. The pH values of peanut shell and corncob bio-oil were found to be 4.7 and 4.5 before the upgrade which further constitutes the problem of bio-oil. The use of the liquid-liquid extraction method of upgrade with the aid of suitable solvent of n-hexane and ethanol improved the oxidation stability, viscosity, and acidity of the peanut shell and corncob bio-oils thus solving the transportation and storage problem of the bio-oil. Conclusively, for the extraction process, it was found that the higher the temperature, the higher the oil yield and vice-versa. The yield of the bio-oil was reduced at a temperature higher than the temperature of the solvent in which the relationship between the process parameters with oil yield and pH was established with the aid of the Box-Benken response surface method. The pH adjustment is further justified with the addition of Sodium hydroxide (NaOH), thus facilitating wider application of the bio-oil as acidity is reduced. The experimental run shows that n-hexane was more effective than ethanol in the extraction of bio-oil.

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