

Production of Bio-Oil from Agriculture Waste

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Abstract

Biomass energy which includes producing energy fuel from plant is considered a promising source of renewable energy. This research aims to develop a new method to liquefy two types of agriculture waste and compare between their produced bio-oils in terms of ultimate production conditions, compositions and applications.

Firstly, One gram of two different types of agriculture wastes include Corn sticks (CS) and Palm leaves (PL) were liquefied by autoclaving at 2.5 atm pressure and 220°C temperature. The liquefaction process had been performed in the range of 10 to 80 ml ethanol/g treated solid, and retention time ranges between 10 to 120 min., the produced bio-oil were extracted and separated into three fractions: volatile, light and heavy.

The results show that, the maximum amount (0.04 g/g) of volatile bio-oil can be produced from CS at 40 ml ethanol/g treated solid and 30 min retention time. However maximum amount of light bio-oil (g/g) was obtained from CS at 30 ml ethanol/1 g treated solid and 60 min retention time. For heavy bio-oil, maximum amount (0.25 g/g) was derived from CS when the ratio between ethanol (ml): treated solid (g) is 30:1 and the retention time is 60 min.

Experimental data had been analysed using matlab software to get the modules which give the relations between bio-oil produced, ethanol to solid ratio and retention time in order to get the ultimate conditions of the process. GC-MS and FTIR analysis has been done to identify the bio-oils compositions. The results show that produced bio-oil from CS is highly contained carbon atom from C20-C38 in addition it contains high percentage of C6-C9 atoms. Therefore, the bio-oil from CS can be used as bio-fuel. However, the produced bio-oil from PL is mainly unsaturated acids which has carbon atom from C10-C18. Thus, it has pharmaceutical applications.

Keywords: Bio-oil; Agriculture waste; Bio-fuel

Introduction

The current energy resources have limited reserves and are decreasing with increasing world population and fasting in developing technology [1]. The biomass resources are abundant all over the world [2]. The local utilization of biomass especially the residual biomass from agriculture is very low and the unused residual had been get rid of by unfriendly environmental way by burning these residual in field and produced black cloud saturated with carbon dioxide [3,4]. Renewal and abundance advantages of biomass make them attractive source for renewable energy. Biomass energy "bioenergy" which are producing biofuel and energy using plant is considered a promising technique as it has a recycled array [2].

Corn consider essential foods in many parts of the world, the annual global production is 864.96 million metric ton, respectively. These cultivations produce yearly residues (leaves, stalk, straw) a proximately 1730 million metric ton [5]. The total amount of date palm trees all over the world is around 100 million [6]. In Egypt the total amount of agriculture residues from Corn reaches about 7.3 million ton of dry matter per year [5], and it has 16 million trees of date palm approximately. Every date palm under normal growth conditions formed an average 12-15 new leaves consequently the same amount can be expected to be cut as part of the maintenance of the palm [6]. Expected calculated amount of palm leaves (take weight of one dry leaf approximately 5 g) nearly 2.88 million kg of dry leaves many researches were done to produced bio-fuels from biomass by thermochemical conversion which offers a high range of technologies, the main principle can be used are: i) Direct liquefaction which refers to conversion of biomass to biofuel by means of using solvent with or without catalyst in one step without gasification's and synthesis intermediate steps using. This would be the most efficient way to produced fuel. ii) Indirect liquefaction which used synthesis gas generated from biomass gasification to produced high quality synthetic fuel [7]. Using of fast pyrolysis to produced bio-oil

depend only on wood biomass no other agriculture waste [8-10]. Many solvent were used during liquefaction process such as water, ethanol, methanol and acetone. Although water is environmental friendly but Lie et al. [11] found that the bio-oil produced from biomass in water solvent have lower carbon content with low heating value. The role of solvent in liquefaction process is considering hydrogen donor in the reaction which induced a strong medium for destroying biomass molecular structure in addition increasing the yield of the liquid [11]. Biomass liquefaction is thermal-chemical reactions where macromolecular substances are decomposed into small molecules under heating conditions and in the presence of catalyst. During this process, lots of reactions occurred such as cracking, hydrogenation, hydrolysis and dehydration [12,13]. This can't define by single reaction step as the combination of cellulose, hemicellulose and lignin which interacts with each other leading to very complex chemistry [14].

Bio-oil is a kind of liquid fuel made from biomass materials such as agricultural crops, algal biomass, municipal wastes, agricultural and forestry by-products via thermo-chemical processes [15,16]. As one kind of new inexpensive, clean and green bio-energies, bio-oil is considered as an attractive option instead of conventional fuel in the aspect of reducing environmental pollution [17-19]. Bio-oil produced from rice straw contains high present of light constituents (C16-C19)

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Received: August 04, 2017; **Accepted:** January 17, 2018; **Published:** January 26, 2018

Citation: Mohamed OA (2018) Production of Bio-Oil from Agriculture Waste. Biochem Anal Biochem 7: 348. doi: 10.4172/2161-1009.1000348

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and small parent of volatile bio-oil and heavy bio-oil [20]. The maximum amount of volatile, light and heavy bio oil produced at 30 ml ethanol/g rice straw and retention time equal 60 min [20]. The bio-oil obtained from rice straw constituents mainly from esters groups which can use as bio-fuel [20].

Experimental Section

Materials preparations

Rice straw, corn sticks, palm leaves, the samples were milled then dried at 105°C for 24 h. the dried biomass powder was first extracted with chloroform/ethanol (2/1 v/v) for 6 h, and the meal was allowed to dry in an oven at 80°C for 24 h, then treated by NaOH 7.5% for 2 h and 17.5% for 2 h after that washed with distilled water until pH of washed water up to 7 then dried at 80°C for 24 h to remove the extractable materials [20-22].

Liquefaction method

The liquefaction experiments were carried out using autoclave at a working pressure 2.5 atm and working temperature 220°C, the different solid to ethanol ratio studied at constant time by using 5 g of treated each solid and added to each one 100, 200, 300, 400 ml ethanol, the volatile, light and heavy types of produced oil extracted by water then by Acetone and distilled these are done at 15 min, then all repeated at 30 min, 60 min and 90 min. to Studied the effect of time on liquefaction process.

Experimental analysis

The Bio-oil produced were separated from the solvents by vacuum distillation then collected to analysis by using mass spectrophotometer gas chromatography model perkin elmer At acquisition parameters. Oven: Initial temp 45°C for 1.50 min, ramp 15°C/min to 300°C, hold 11.50 min, Inj=250°C, Volume=0 L, Split=20:1, Carrier Gas=He, Solvent Delay=3.00 min, Transfer Temp=280°C, Source Temp=300°C, Scan: 43 to 500 Da, Column 30.0 m × 250 m [15,20,23]. Either analysis by Fourier transformer infrared (FTIR) spectrophotometer with MCT detector and spectra region from 600-4000 cm⁻¹ [20,24,25].

Result and Discussion

Studying the effect of ethanol biomass ratio

The conditions used in these experiments were selected to examine the effect of ethanol biomass ratio 10, 20, 30, 40, 60 (ml ethanol/g biomass) on the bio oil production (Volatile bio-oil, Light bio-oil,

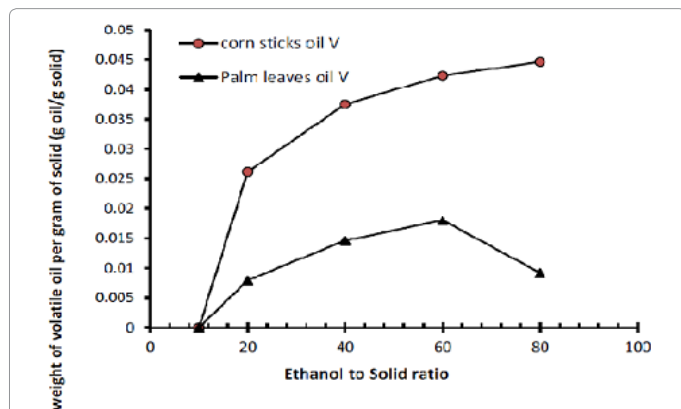


Figure 1: Relation between ethanol solid ratio and amount of volatile oil produce per gram solid at 30 min retention time.

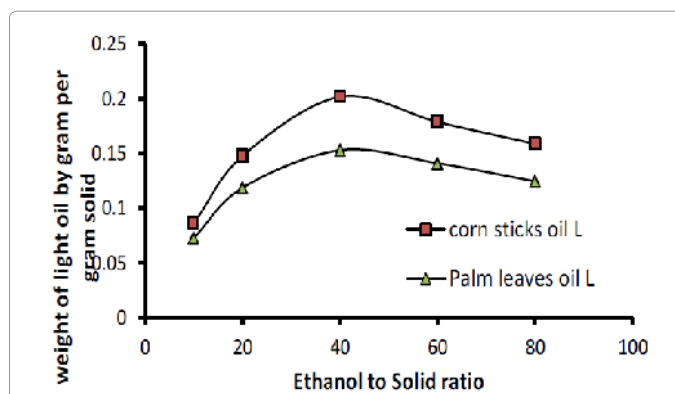


Figure 2: Relation between ethanol solid ratio and amount of light oil produce per gram solid at 30 min retention time.

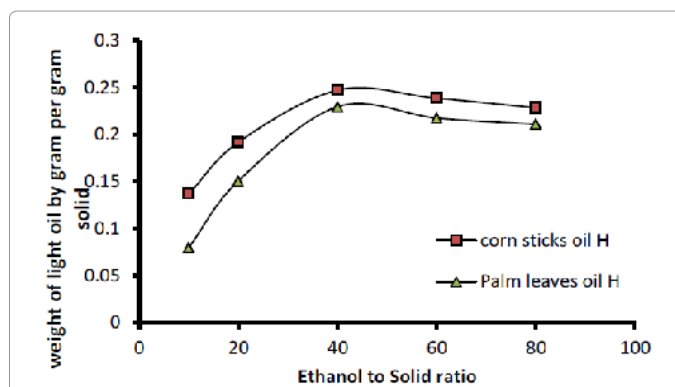


Figure 3: Relation between ethanol solid ratio and amount of heavy oil produce per gram solid.

Heavy bio-oil) for time equal 15 and 30 min. The data obtained in Figures 1-3.

From Figures 1-3, we find that, increasing in ethanol to biomass ratio increase production of bio-oil but this effect difference from volatile, light and heavy bio oil corn sticks and palm leaves.

As increasing in ethanol to biomass ratio increase the production of volatile bio-oil the major amount obtained from corn sticks (0.0447 g v. oil/g corn sticks) then palm leaves (0.00919 g v. oil/g palm leaves) [26].

The major function of ethanol during the liquefaction process were to provide active hydrogen, and free radicals [27] this broke the C-C and C-O ponds in cellulose molecules and forming Sorbitol which convert to alkanes and alkenes [24] with more hydrogenation this increase the amount of volatile material (volatile bio oil) with increasing ethanol to biomass ratio.

In opposite for liquid and heavy bio-oil production increase with increasing the ethanol to biomass ratio until reach maximum at 30 ml ethanol/gram solids after that increase ratio decrease the production of light and heavy bio oil this due to degradation occurs for intermediate compound [23]. The maximum amount of light bio-oil (g bio-oil/g biomass) obtained at 30 ml ethanol/gram biomass was taken from Palm leave 0.1749 then from corn stick 0.1528 g/g.

The maximum amount of heavy bio-oil (g bio-oil/g biomass) was obtained from corn stick 0.247 g heavy oil/g corn stick then from palm leaves 0.029 g/g.

Studying the effect of retention time in bio-oil production

Figures 4-8 shows the effect of retention time on amounts of bio-oil production in the liquefactions of the three agriculture waste (rice straw, corn sticks and palm leaves) at 2.5 atm and 220°C. The produced amount of volatile bio oil reach to maximum at 30 min after that any increase in retention time decrease the amount of volatile oil these is due to recombination and re-polymerization of reactive fragments

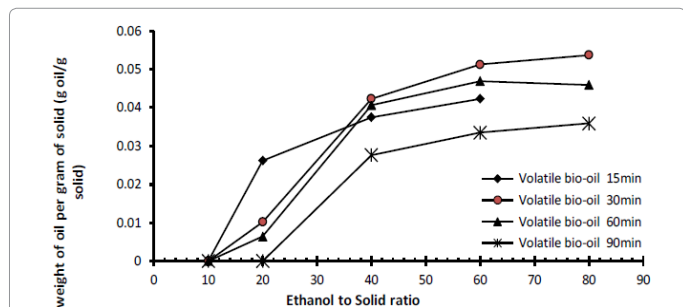


Figure 4: Amount of volatile oil (g) per gram corn sticks at different autoclaving time for rice straw.

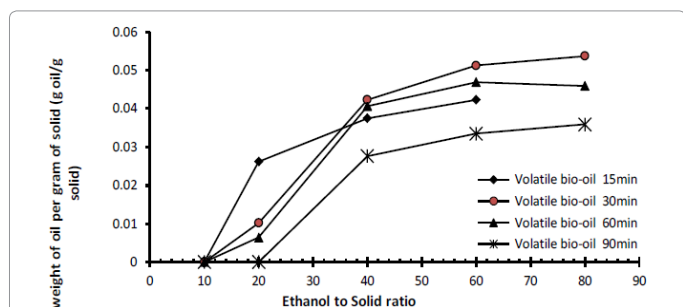


Figure 5: Amount of volatile oil (g) per gram palm leaves at different autoclaving time for rice straw.

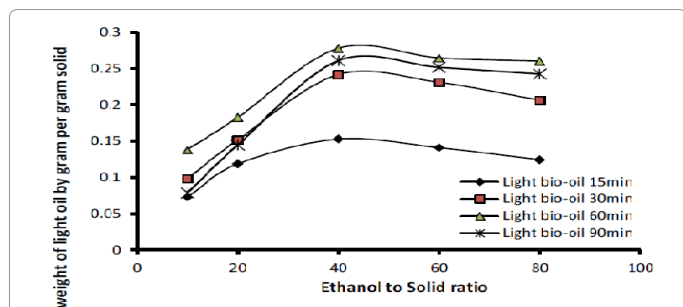


Figure 6: Relation between ethanol solid ratio and amount of light oil produce per gram palm leaves at different autoclaving time.

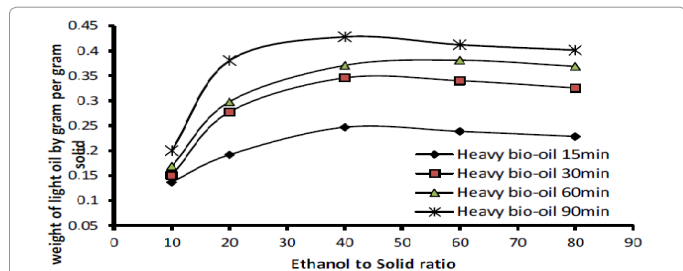


Figure 7: Relation between ethanol solid ratio and amount of heavy oil produce per gram corn sticks at different autoclaving time.

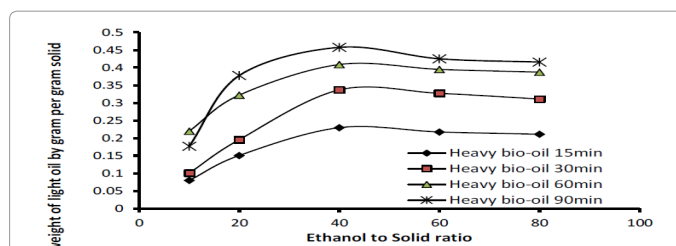


Figure 8: Relation between ethanol solid ratio and amount of heavy oil produce per gram palm leaves at different autoclaving time.

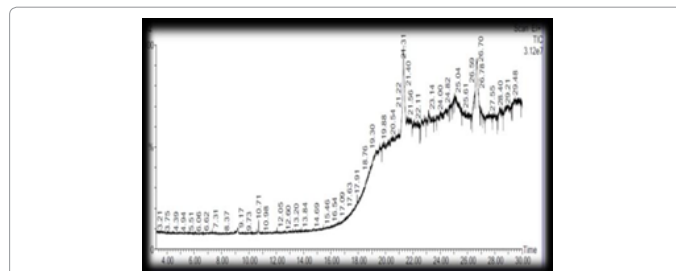


Figure 9: Chromatogram of corn sticks bio-oil by using Gas chromatograph with mass detector.

RT	Area %	Compound Name	N%	Chemical formula
21.311	8.678	Oleic acid, 3-(octadecyloxy)propyl ester	100	C ₃₉ H ₇₆ O ₃
19.405	6.212	1-Monolinoleoylglycerol trimethyl ether	71.58	C ₆ H ₁₄ O ₃
26.688	5.355	Cyclopropane, octadecamethyl-	61.71	C ₂₁ H ₆₀
20.22	3.174	(t-Butyl-dimethyl-[2-methyl-2-(4-methyl-pent-3-enyl)-cyclopropyl]-methanol	36.58	C ₉ H ₁₈ O
19.58	3.114	Stearic acid, 3-(octadecyloxy)propyl ester	35.89	C ₃₉ H ₇₈ O ₃
19.875	2.83	3H-3,10a-Methano-1,2-benzodioxocin-3-ol, octahydro-7,7-dimethyl-, (3a,6a,10a)-	32.61	C ₂₆ H ₅₂ O
25.042	2.4	Butanoic acid, 1a,2,5,5a,6,9,10,10a-octahydro-5ahydroxy-4-(hydroxymethyl)-1,1,7,9-tetramethyl-6,11-dioxo-1H-2,8amethanocyclopenta[a]cyclopropa[e]cyclodecen-5-yl ester, [1aR-(1a,2a,2a,5a,5a,8a,9a,10a)	27.66	C ₂₇ H ₅₄ O ₃
24.482	2.296	Stearic acid, 3-(octadecyloxy)propyl ester	26.46	C ₃₉ H ₇₈ O ₃

Table 1: The main component of corn sticks bio-oil from gas chromatography.

[20]. By comparison the two agriculture waste (corn sticks and palm leaves) find that the maximum amount of volatile oil produce at 30 min and the minimum amount at 120 min.

For light bio-oil first the amount of light oil produced increase with time until reach the maximum at 60 min after that the amount of light decrease with increasing time the minimum amount at 90 min. At the start time the reactions of depolymerization of the biomass, and decomposition of the biomass monomers by cleavage, dehydration, decarboxylation and deamination occurs so the amount of light bio-oil increase with time until reach maximum after that increasing time make the reactive fragments recombination and repolymerization this make it large molecules and heavy oil.

Produced amount of heavy bio oil increase with increasing retention time and reach to maximum at 90 min this is due to recombination and re-polymerization of reactive fragments.

GC-MS Analysis

The identification of the major components of the three types of bio-oil through GC-MS is shown in Figures 9, 10, Tables 1 and 2.

$$0.0003373y^2+1.359 \times 10^{-6}x^3-5.024 \times 10^{-7}x^2-1.638-10^{-7}xy^2+1.881 \times 10^{-6}y^3 \quad (2)$$

Goodness of fit

SSE: 0.0007673; R-Square: 0.9874; Adjusted R-square: 0.9646; RMSE: 0.01239.

Goodness of validation

SSE: 0.0007673; RMSE: 0.01239.

Linear module for heavy bio oil

$$Z_{h, \text{corn}} = -0.01811+0.006373X+0.01607 Y-0.00001177x^2+6.413 \times 10^{-5}X*Y-0.000736 Y^2+730 \times 10^{-7}X^3-1.73 \times 10^{-7}X^2Y-7.804 \times 10^{-7}XY^2+1.174 \times 10^{-6}Y^3 \quad (3)$$

Goodness of fit

SSE: 0.0001781; R-Square Adjusted: 0.9985; R-Square: 0.9957; RMSE: 0.005969.

Goodness of validation

SSE: 0.0001781, RMSE: 0.005969.

For Palm leaves

The natural and coded variables were determined and are presented in Table 4.

Linear module for volatile bio oil

$$Z_{l, \text{palm}} = 0.02534+0.001302x+0.001209y-2.605 \times 10^{-5}x^2-2.17 \times 10^{-7}x^3y-1.542 \times 10^{-5}y^2+1.639 \times 10^{-7}x^3-8.407 \times 10^{-8} x^2 Y-1.109 \times 10^{-7}xy^2+2.766 \times 10^{-8}y^3 \quad (4)$$

Goodness of fit

SSE: 0.00001248; R-Square: 0.986; Adjusted R-Square: 0.9609; RMSE: 0.00232.

Goodness of validation

SSE: 0.00001248; RMSE: 0.00158.

Linear module for Light bio oil

$$Z_{l, \text{palm}} = -0.04436+0.00437X+0.007127Y-6.927 \times 10^{-5}X^2+7.759 \times$$

X1	y	x1 (time, min)	y (Ratio)	Volatile	Light	Heavy
-1	-1	15	15	0.00413	0.1006	0.11215
1	-1	90	15	0	0.1215	0.2765
0	-1	52.5	15	0.00465	0.1571	0.2398
-1	1	15	90	0.00488	0.11655	0.2077
1	1	90	90	0.01577	0.2379	0.4112
0	1	52.5	90	0.02215	0.2418	0.3632
-1	0	15	52.5	0.01673	0.1478	0.2247
1	0	90	52.5	0.007	0.2607	0.4825
0	0	52.5	52.5	0.02295	0.2629	0.3833
0.5	-1	71	15	0.00117	0.1466	0.2731
0.5	0	71	52.5	0.01555	0.2657	0.4096
0.5	1	71	90	0.0178	0.2582	0.4103
-1	0.5	15	71	0.01315	0.1332	0.2139
1	0.5	90	71	0.01214	0.2495	0.4225
0	0.5	52.5	71	0.02356	0.2528	0.3729

Table 4: Range and levels of natural and corresponded coded variables for bio oil from palm leaves.

$$10^{-5}X*Y-0.0001375Y^2+2.558 \times 10^{-7}X^3-2.337 \times 10^{-7}X^2Y-3.384 \times 10^{-7}XY^2+7.198 \times 10^{-7}Y^3 \quad (5)$$

Goodness of fit

SSE: 0.0001195; R-Square: 0.998; Adjusted R-Square: 0.994.

Goodness of validation

SSE: 0.0001195; RMSE: 0.004889.

Linear module for heavy bio oil

$$Z_{h, \text{palm}} = -0.1544+0.0059X+0.01607 Y-6.472 \times 10^{-5}X^2+6.726 \times 10^{-5}X*Y-0.0002925 Y^2+2.572 \times 10^{-7}X^3-1.447 \times 10^{-7}X^2Y-4.444 \times 10^{-7}XY^2+1.622 \times 10^{-6}Y^3 \quad (6)$$

Goodness of fit

SSE: 0.001537; R-Square: 0.9902; Adjusted R-Square: 0.9726.

Goodness of validation

SSE: 0.001537; RMSE: 0.00158.

Results and Discussion

Examination of the table shows that the models is highly correlation coefficient (R2)>0.9, the model fits the experimental data fitted with a third-order polynomial model (eqns. (1)-(6)), the model being rejected if the R2 value is less than 0.8 [32]. The 3D surface plotted in Figures 13-23 show that the combination reaction time, min and 100 ethanol/solid ratio significant effects volatile bio-oil (g/g). Figures demonstrate that the increase in reaction time, min with the increase in liquid/Solid ratio concentration enhance the efficiency of volatile bio-oil weight production until reach the maximum then the production rate decrease as a result of re-polymerization but we find that the rate of production of volatile bio-oil is very small, comparison with the rate of production of light and heavy bio-oil [33-39].

In the similar way, the 3D surface plotted to light bio-oil production

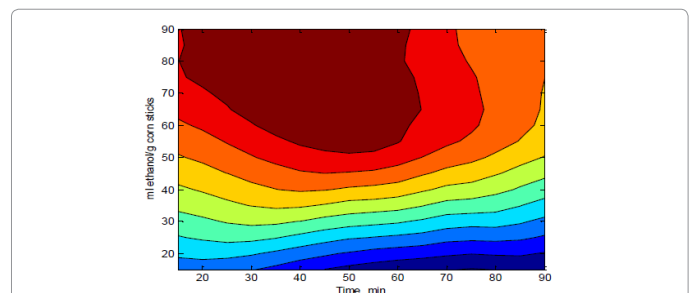


Figure 13: Contour plot for volatile bio-oil produced from corn sticks versus difference in time and ethanol/solid ratio.

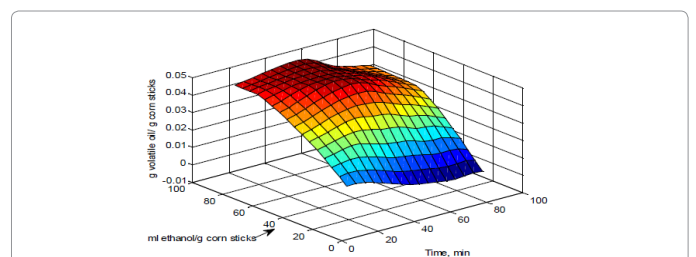


Figure 14: Surface plot for volatile bio-oil produced from corn sticks versus difference in time and ethanol/solid ratio.

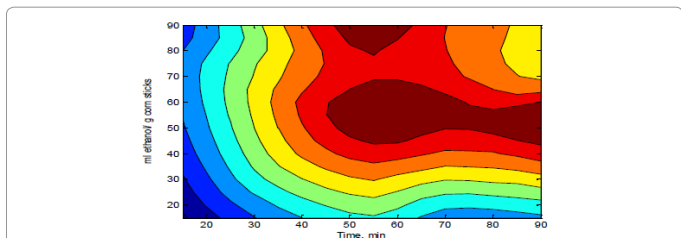


Figure 15: Contour plot for light bio oil produced from corn sticks versus different time and ethanol/solid ratio.

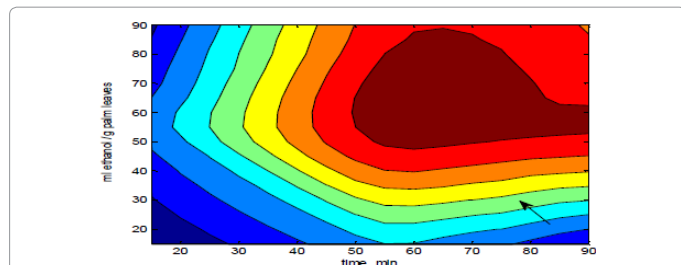


Figure 20: Contour plot for light oil produced from palm leaves versus time and ethanol/solid ratio.

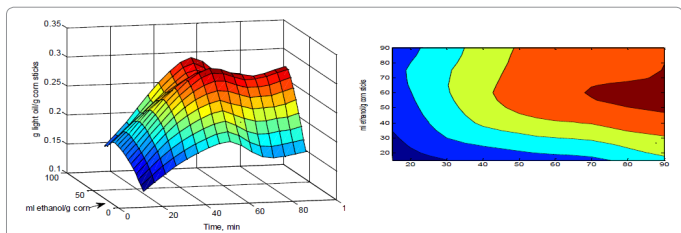


Figure 16: (A) surface plot for light oil produced from corn sticks versus different time and ethanol/solid ratio (B) contour plot for heavy oil produced from corn sticks versus different in time and ethanol/solid ratio.

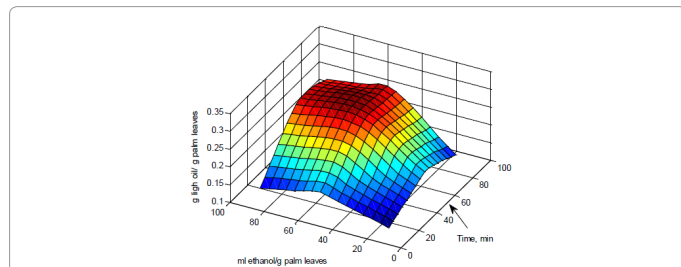


Figure 21: Surface plot for light oil produced from palm leaves versus time and ethanol/solid ratio linear module for heavy bio oil.

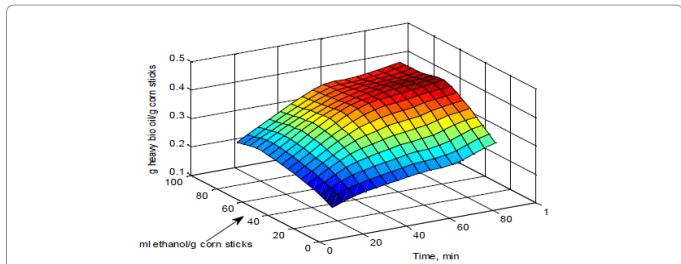


Figure 17: Surface plot for heavy bio-oil produced from corn sticks versus different in time and ethanol/solid ratio.

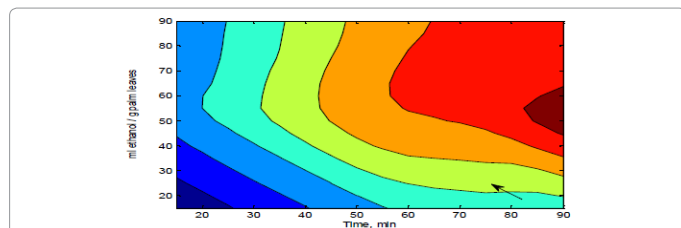


Figure 22: Contour plot for light oil produced from palm leaves versus time and ethanol/solid ratio.

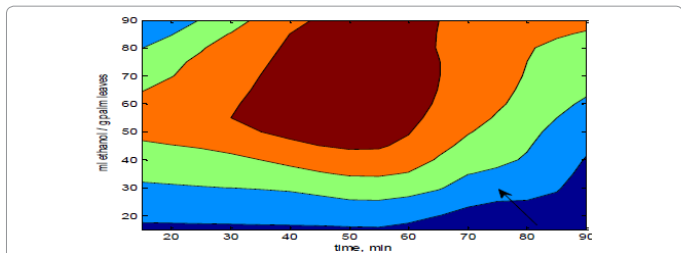


Figure 18: Contour plot for volatile oil produced from palm leaves versus time and ethanol/solid ratio.

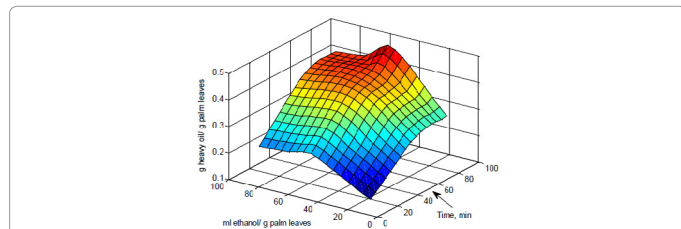


Figure 23: Surface plot for heavy oil produced from palm leaves versus time and ethanol/solid ratio.

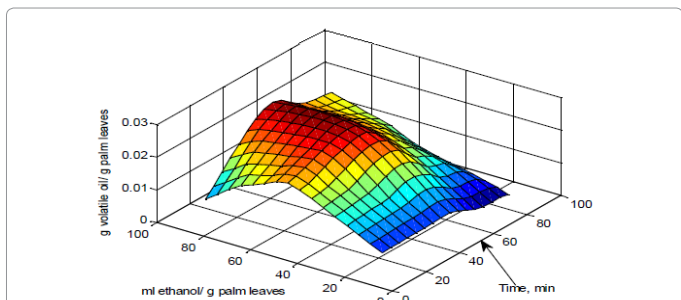


Figure 19: Surface plot for volatile oil produced from palm leaves versus time and ethanol/solid ratio.

shows that the combination Reaction Time, min and liquid/solid ratio has a significant effects on Light bio-oil production these figures demonstrates that the increase in Reaction Time, min with the increase in liquid/solid ratio enhance the efficiency of light bio-oil production until reach the maximum then the production rate decrease.

For heavy bio-oil production the figures demonstrate that the increase in Reaction Time, min with the increase in liquid/solid ratio enhance the efficiency of heavy oil production rate until reach the maximum. Either any increase in reaction time, increase the rate of polymerization and combination which increase the rate of heavy-oil production.

Response surface analysis was used to determine optimum conditions of the operating variables in the production of bio-oil (Table 5) [20].

Raw material	Bio-oil type	Time, Min	Ethanol/Solid (l/g)	Bio-oil Produced g oil/g solid
Rice straw	Volatile	38	42	0.02975
	Liquid	52.5	35	0.2450
	heavy	52.5	35	0.237
Corn sticks	Volatile	38	42	0.0464
	Liquid	52.5	35	0.2106
	heavy	52.5	35	0.2470
Palm leaves	Volatile	38	42	0.0131
	Liquid	52.5	35	0.2549
	heavy	52.5	35	0.0318

Table 5: Optimum conditions for all types produced of bio oil by using matlab7.

Conclusions

•The result of that investigation reveals the production of bio-oils from agriculture waste.

•The optimum conditions of producing light and heavy bio-oil are ethanol to solid ratio 30 ml/g and at 60 min retention time but for volatile bio-oil the best conditions are 40 ml ethanol/g solids and 30 min.

•The characteristics of bio-oil which produced from corn sticks contain high present of heavy constituents C20-C38 and high percent of volatile bio-oil T C6-C9 than Bio-oil produced from Palm leaves.

•The characteristics of bio-oil which produced from palm leave mainly unsaturated acids C10-C18.

•The optimum amount of volatile, light and heavy bio oil produced from corn sticks at optimum conditions are 0.0447 g volatile oil/g corn sticks, 0.1749 g light oil/g corn sticks and 0.247 g heavy oil/g corn stick

•From GC-MS and FT-IR analysis the bio-oil produced from corn stick are ester and Alkanes groups which use either as biofuel and bio oil from palm leaves are unsaturated fatty acids (Linoleic acid and tetradecenoic acid) which are have a lot of applications in pharmaceutical industry either it contain Octadecanesulphonyl chloride which use in dyes industry.

• Statistical analysis by matlab7 software's is studied for the factors and response and the related equation are obtained.

• The optimum conditions are obtained from matlab 7 for light and heavy bio oil produced are 52.5 min for retention time and 35 ml/g ethanol/solid ratio, but for volatile bio oil the optimum conditions are 38 min for retention time and 42 ml/g ethanol/solid ratio, which is near to the experimental work.

• To obtain the relation between the two factors for every response find by Surface plot.

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