Article

Open Access

FAST PYROLYSIS OF JATROPHA SEEDS IN A FIXED BED FURNACE

Shaimaa Saeed^{1,*}, Ibrahim Ashour^{1,} Mohamed R. O. Ali²

¹ Department of Chemical Engineering, Elminia University, Egypt

² Department of Mechanical Power Engineering and Energy, Elminia University, Egypt

Received October 20, 2019; Accepted December 12, 2019

Abstract

The biomass, which converted into alternative fuel, has become an attractive source of renewable energy because of the shortage and high prices of fossil fuels. The bio-energy is now accepted as having the potential to provide the major part of the projected renewable energy in the future. Pyrolysis is one of the three main thermal paths, along with gasification and combustion, for providing useful and valuable bio-fuel. The present work will consider Jatropha curcas seeds as the biomass source because Jatropha seeds have high energy bearing seeds available in nature. The fast pyrolysis of Jatropha was carried out in a fixed bed batch reactor made up of stainless steel at a temperature ranging from 400°C to 550°C to produce liquid biofuel at an interval of 50°C. The effect of temperature on the fast pyrolysis of the material is studied to know the optimum temperature for maximum liquid yield. The thermal degradation of the Jatropha seed was studied using thermogravimetric analysis (TGA) at a heating rate of 20°C which indicated the range of temperature in which the rate of decomposition is maximum. Calcium oxide nano catalyst derived from waste eggshells was used to study the effect of using a catalyst in the fast pyrolysis of Jatropha seeds. The oil and catalytic oil were obtained at optimum temperatures analyzed according to their elemental analysis, fuel properties, functional groups present, and com-pounds' presence. The result so obtained is compared with the commercial fuel. The chemical compositions of the bio-oils were investigated using FTIR and GC-MS. Properties of CaO catalyst were studied using EDX, SEM and XRD analyses.

Keywords: Fast pyrolysis, Jatropha seeds, Catalyst, Modeling, TGA, Activation energy.

1. Introduction

The biomass is now being examined as an important alternative fuel all over the world. There are many sources of biomass being considered as a potential standard of fossil fuel and chemical feedstock. It has the potential to provide 10–14% of the world's total energy utilized daily ^[1]. Pyrolysis is a valuable economic conversion thermal process for solid wastes into alternative fuels into solid fuel char, liquid bio-oil, and gases ^[2]. The pyrolysis parameters such as time and heating rate can eliminate the type of the process into slow pyrolysis and fast pyrolysis. At the slow pyrolysis, the heating rate is (less than 10° C/s), the reaction rate has occurred with slow heat transfer rate, and the retention time is relatively long time ^[3]. Usually, slow pyrolysis is used for charcoal production. Furthermore, the fast pyrolysis has occurred at a high heating rate up to 100°C/s and short retention time less than 2 seconds ^[2]. The fast pyrolysis process in most cases is produced 45–75wt% of liquid fuel, 15–25 wt.% of solid residues, and 10–20 wt.% of gases, depending on the feedstock and pyrolysis parameters used. In general, pyrolysis products are interested in using as a primary fuel. While there was a lot of researches [4-5] interested in studying the effect of pyrolysis's parameters on increasing the yield of pyrolytic liquid fuel, which shows similarity as an alternative fossil fuel. since the pyrolytic liquid fuel or bio-oil produced from the pyrolysis process is contained a lot of oxygenated compounds, the Bio-oil fuel properties weren't conformed to the standards of fossil fuels ^[6]. So, it is recommended to use a catalyst to enhance the fast pyrolysis process ^[7]. Due to the various usages of pyrolysis products and especially the scope implementation of

bio-oil, the recent study is concentrated on the fast pyrolysis of Jatropha seeds, which is adequate to produce a high proportion of the liquid bio-oil product. Here the form of biomass to be used is the Jatropha seed. This plant grows wildly in many areas all over the world and even found on infertile soil. The *Jatropha curcas* is a plant that is usually grown as a source of bio-oil. The seeds are the basic source of oil extraction. Because of its toxicity, they are not utilized by humans. Therefore, the prime goal of the jatropha cultivation is extracting jatropha oil ^[8].

2. Materials and experimental apparatus

The Jatropha seed samples used as feedstock were collected. These seeds were crushed into small sizes and kept in the oven for about 5-6 hours at a temperature of 60-70°C.

The catalyst has been prepared from eggshells. Eggshells were first washed with water repeatedly to remove impurities and then dried in drying oven at 110°C for about 24 hours. The dried shells were grounded to a fine powder to uniform size of the sifted flour using a sieve of 200 mesh sieve and the result is used as raw material for the synthesis of catalyst. The calcination of eggshells powder was done in a muffle furnace at 900°C for about 2 hours.

The thermogravimetric analysis (TGA) of raw material has been done using the DTG 60 instrument. TGA was done at a heating rate of 20°C/min. The sample was heated up to a final temperature of 700°C.

Proximate analysis (using ASTM) is the determination of moisture, volatile matter, fixed carbon (by difference) and ash by prescribed Methods. The ultimate analysis of the material was carried out in CHNS elemental analyzer (Vario El Cube Germany) to know the elemental composition.

2.1. Reactor specification

The experimental setup consists of a cylindrical fixed bed batch reactor with the electrically heated furnace, condensation system, nitrogen gas cylinder, PID controller, and biomass feeding and char removing the system (Fig. 1.).



Figure 1 Experimental apparatus of the pyrolysis process

The reactor was made of 304 stainless steel with 11 cm internal diameter and 40 cm height. The reactor was externally heated by the electrical furnace with 2.5 kW power, which insulated to reduce the heat loss. A K-type thermocouple was inserted inside the reactor to measure the pyrolysis temperature. The temperature inside the reactor was maintained constant by using a PID controller. The nitrogen tank was used to supply N₂ gas, which used to

create an inert condition inside the fixed bed reactor and sweeping the pyrolysis vapors from the reactor to the condensers. The reactor was connected to three condensers (one stainless steel and two glass condensers) and the condensed liquid was collected in a collecting flask at the end of each condenser and weighted for yield. The flask of the first condenser was immerged into the ice cooling bath to increase the condensation efficiency. the feeding system consists of feeding hopper, screw feeder and water-cooling jacket to prevent the decomposition of biomass before the heating zone. After the pyrolysis process, the reactor was cooled and char was removed from the reactor by using the screw removing system and collected and weighed.

2.2. Pyrolysis procedures

Pyrolysis experiment was carried out for Jatropha seed at different temperatures starting from 400°C to 550°C at 50 intervals. The experiment could continue for at least 30 min after the oil production stopped. For each sample run amount of liquid produced and char remained in the reactor were noted. The temperature at which the amount of liquid fuel production became maximum is the optimum temperature.

The liquid products were condensed by using a water bath. The temperature is measured by Fig.1 shows the schematic diagram of the pyrolysis experimental set-up. Water is circulated as a cooling medium in the condenser. The liquid product collected in the measuring cylinder contains liquid fuel and oily water. This oily water is basically water with some dissolved nitrogen and oxygen containing hydrocarbons.

A Perkin-Elmer infrared spectrometer analyzer was used to determine (FTIR) analysis of pyrolytic oil obtained at a temperature of 500°C in the range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹ to know the presence of various functional groups with and without using CaO catalyst. Furthermore, GC-MS-OP 2010 [SHIMADZU] analyzer was used to analyze the pyrolytic oil at 500°C to find out the chemical compounds present in the pyrolytic oil and to study the effect of using CaO catalyst on the JCSPO. The ultimate analysis of the pyrolytic char was done to find out their average pore diameter.

3. Results and discussions

The results of proximate and ultimate analyses of *Jatropha curcas* seed (JCS) sample and its pyrolysis oil. It can be seen from Table 1 that JCS samples are characterized by high volatile matter (85%), which makes it more readily devolatilized than solid fuel. So, the release of less fixed carbon makes them more useful for pyrolysis and gasification. Also, there are small amounts of moisture, ash, and a higher weight percentage of oxygen followed by carbon and hydrogen with no sulphur content. The biomasses with high heating values make them very attractive for the source-feeds for clean energy production instead of fossil-based solid fuels, as demonstrated in Table 1. High carbon and low oxygen in JCS as compared to coal are favorable for combustion applications, while the higher proportion of carbon (relative to hydrogen and oxygen content) increases the energy content of fuel because energy contained in carbon-carbon bonds is greater than that of carbon-oxygen and carbon-hydrogen bonds.

Composition\raw material	Units	Jatropha seed
Volatile matter	%wt	86.5
Moisture	%wt	04.5
Ash content	%wt	04
Fixed carbon	%wt	05

Table 1. Proximate analysis of Jatropha seed

Table 2. Ultimate analysis of Jatropha seed

Material	Carbon	Hydrogen	Nitrogen	Sulphur	C/H	C/N
composition	%	%	%	%	ratio	ratio
Jatropha seed	56.55	4.23	4.68	Nil	12.33	12.08

3.1. Characterization of the catalyst

The morphology of the eggshell waste-derived catalyst was investigated by SEM, as shown in Figure 2 (a), (b), (c), and (d). According to the SEM images, the calcined chicken eggshell waste typically comprises the irregular shape of particles. The smaller size of the grains and aggregates could provide higher specific surface areas.



Figure 2. The SEM image of calcium oxide powder surface (a) 750 x magnification, (b) 3300x magnification, (c) 6500x magnification and (d) 22000x magnification



Figure 3. XRD pattern of calcium oxide powder surface

XRD spectra of calcined chicken eggshell samples were obtained with Cu radiation (λ =0.154056 nm) at 30 kV, 30 mA, a scan speed of 2°/minute, and a scan range of 5-60°. The decomposition products of chicken eggshell at the variation of temperature were identified using XRD powder as shown in Figure 3.

The data from Figure. 2 are compared to the XRD pattern of the shell after decomposition at the XRD pattern of CaO

from the Joint Committee on Powder Diffraction Standards (JCPDS) file. It can be seen that powder has high crystallinity and sharp spectra. There are sharp peaks on the fabric coated CaO, at 2-theta of 32.3401; 37.3924; 53.8966, these peaks obtained from calcined eggshells are similar to calcium oxide data collected by JCPDS ^[9].

	1	,			
CaO			2(θ°)		
In this research	32.292	37.604	54.233	64.678	67.861
JCPDS 772376 (1997)	32.2	37.3		64.1	67.3
Literature [9-10]	32.2	37.4	53.9	64.2	67.4

3.2. Thermo gravimetric analysis of raw materials (TGA)

Figs 4 and 5 show experimental TG (thermogravimetric)–DTG (derivative thermogravimetric) curves for thermal decomposition of JCS with and without catalyst under an atmosphere of nitrogen at the heating rate of 293K min⁻¹.





Figure 4. TGA thermograph of Jatropha seed with and without using catalyst

Figure 5. DTG thermograph of Jatropha seed with and without using catalyst

Consistent with, Figs. 4-5 the moisture was removed from raw materials up to (306-312)K, and main decompositions of investigated samples started around 307 K and finished around 873K. the TG-DTG curves (Fig 3-4) show three distinct mass loss stages could be determined $(\Delta TI = 306-535K, \Delta TII = 535-689K, and \Delta TIII > 689K, respectively), and it is in agreement$ with researches related to JCS. The 1st. stage decomposition represents the evaporation of moisture contents, 2nd decomposition indicates the formation of volatiles mainly. In the 3rd stage, the pyrolysis residue slowly decomposes, with the weight loss velocity becoming smaller and smaller, and the residue ratio tends to become constant at the end of the hydrocarbon decomposition. Due to the high decomposition rate, the rapid decomposition zone or 2nd stage of decomposition is treated as an active pyrolytic zone. During the 2nd stage, the intermolecular combination and weaker chemical bonds are broken. The side aliphatic chains are broken and some small gaseous molecules are produced because of the lower temperature. During the 3rd stage, chemical bonds are broken at a higher temperature and the parent molecular skeletons are destroyed. As a result, the larger molecule degrades into smaller molecules in the form of a gaseous phase. Finally, char remains [11-16]. In the DTG curves, as noticed from Fig. 2, the initial weight loss rates at heating rate $293K^{-1}$ were fast, accompanied by a big shoulder peak within 368 to 514.7K. The weight loss in this pyrolysis zone made great contributions to the total weight loss (about 74 wt. %) during pyrolysis, Munir et al. ^[17] suggested that the weight loss occurring near 373K represents the initial degradation of lignin and hemicellulose components in biomass. and it was caused by the emission of volatiles from thermal degradation of the three main components in biomass, cellulose, hemicellulose, and lignin. The DTG curves illustrate that the temperature pertinent to the maximum weight loss rate tended to shift to a lower temperature zone. Thus, JCS pyrolysis at a higher heating rate resulted in a complete decomposition.

3.3. Characterization of biofuels

Ultimate analysis of Jatropha seed pyrolytic oil was done to find the elemental composition of bio-oil and are compared with diesel in Table. 4. The CHNO analysis of the pyrolytic oil shows that it contains the maximum amount of C, H, and O. Higher the C/H ratio shows the oil having good calorific value, can be observed from the Tables 4.

Element	Unit	Jatropha seed oil	Diesel
С	%	60.69	85.72
Н	%	8.67	13.2
N	%	3.02	0.18
S	%	Nil	0.3
0	%	27.62	0.6
H/C molar ratio	-	7	1.85
Calorific value	(MJ/kg)	14.63	43.8

Table 4. Ultimate analysis of Jatropha seed pyrolytic oil

FTIR is an important analysis technique which detects the presence and the various characteristic of functional groups present in the bio-oil. As demonstrated in Tables 5 and 6. The FTIR analysis performed on samples at an optimum temperature 500°C with and without the catalyst. The C-H bending vibrations at 528.28 cm⁻¹ detect the presence of alkenes. C-H stretching at 2922.95, 2856.81 cm⁻¹ shows the presence of alkanes. C-H bending vibrations at 1452.464, 1377.001 cm⁻¹ shows the presence of alkanes. The -NO2 stretching vibrations at 1513.89 cm⁻¹ indicates the presence of nitrogenous compounds. O-H stretching at 3245.317cm⁻¹ shows the presence of H-bonded and water impurities. C=O stretching vibration at 1704.341 indicates the presence of ketones, aldehyde, carboxylic acid, as depicted in Figure 6. The results were found consistent with the literature ^[18] and when compared with GC-MS. Phenol compounds disappear by using CaO catalyst, as demonstrated in Table 6.

Wave number (cm ⁻¹)	Type of vibration	Nature of functional group
3245.317	O-H (stretching)	H-bonded, water impurities
2922.959	C-H (stretching)	Alkanes (aliphatic)
2856.818	C-H (stretching)	Alkanes (aliphatic)
1704.341	C=O (stretching)	Ketones, aldehyde, carboxylic acid
1513.894	-NO2 (stretching)	Nitrogenous compounds
1452.464	C-H (bending)	Alkanes
1377.001	C-H (bending)	Alkanes
1267.026	C-O (stretching) asymmetric	Carboxylic acid
1113.728	C-O bending	Ester
1023.071	C-O (stretching)	Alcohols, ethers, esters, carboxylic acids, phenol
907.641	O-H (bending)	Aromatic compounds
720.019	C-H group (bending)	Methylene groups (cis disubstituted alkenes and aromatic)
528.288	C-H bending	Alkenes

Table 5. Functional groups present in Jatropha seed pyrolytic oil without CaO catalyst ^[18]

Table 6. Functional groups present in Jatropha seed pyrolytic oil with Nano CaO catalyst ^[18]

Wave number (cm ⁻¹)	Type of vibration	Nature of functional group
3779.185	H ₂ O stretching	Water impurities
3255.989	O-H (stretching)	H-bonded, water impurities
2924.768	C-H (stretching)	Alkanes (aliphatic)
2859.034	C-H (stretching)	Alkanes
2347.688	O-H stretching	Carboxylic acids and derivatives
2116.156	C=O (stretching)	Alkanes
1642.681	C=C (stretching)	Alkenes
1556.137	-NO2 (stretching)	Nitrogenous compounds
1447.548	C-H bending/ scissoring	Alkanes
1267.265	C-O (stretching)/asymmetric	Carboxylic acids
1105.793	C-O (bending)	Esters
714.412	C-H group (bending)	Methylene groups (cis disubstituted alkenes and aromatic)
623.989	O-H (bending)	Aromatic compounds

The major compounds of Jatropha seed pyrolytic oil with and without catalyst characterized by GC-MS at a pyrolytic temperature of 500°C were given in Tables 7-8.

Retention time	Area %	Name of compound	Molecular formula
3.8994	9.6732	Toluene	C ₇ H ₈
5.1239	1.371	Hexane, 2,4-dimethyl-	C ₈ H ₁₈
6.3598	3.092	Ethylbenzene	C ₈ H ₁₀
6.6116	1.4479	p-Xylene	C ₈ H ₁₀
7.2868	3.7051	Bicyclo [4.2.0] octa-1,3,5-triene	C ₈ H ₈
7.5557	1.0708	Nonane	C ₉ H ₂₀
10.4739	1.9591	1-Decene	C ₁₀ H ₁₀
10.7314	2.0187	Decane	C ₁₀ H ₂₂
11.4123	0.5669	Dodecane	C ₁₂ H ₂₆
12.305	0.6005	Naphthalene, decahydro-	C ₁₂ H ₂₂
12.448	3.8368	Decane, 2,3,7-trimethyl-	C ₁₃ H ₂₈
12.6082	0.7555	Sulfurous acid, hexyl octvl ester	C ₁₄ H ₃₀ O ₃ S
13.4093	2.1447	1-Decanol	C ₁₀ H ₂₂ O
13.5695	0.7074	Benzoic acid, methyl ester	C ₈ H ₈ O ₂
13.6439	1.818	Undecane	C ₁₁ H ₂₄
13.7068	0.9939	Decane, 3,7-dimethyl-	$C_{11}H_{24}$ $C_{12}H_{26}$
14.3477	0.619	Cyclohexene, 1-pentyl-	C ₁₂ H ₂₆ C ₁₁ H ₂₀
15.2003	0.9148	Benzene, pentyl-	
			C ₁₁ H ₁₆
16.07	2.3076	1-Dodecene	C ₁₂ H ²⁴
16.276	1.5405	Dodecane	C ₁₂ H ₂₆
18.2329	1.9255	Dodecane	C ₁₂ H ₂₆
18.5076	0.9563	1-Tridecene	C ₁₄ H ₂₈
18.6907	0.5122	Tridecane	C ₁₃ H ₂₈
19.2972	0.625	Tridecane, 1-iodo-	
20.7677	1.6625	2-Tetradecene, (E)-	C ₁₄ H ₂₈
20.9337	0.8769	Tetradecane	C ₁₄ H ₃₀
22.8849	1.3892	1-Pentadecene	$C_{15}H_{30}$
22.965	1.265	Tridecane, 1-iodo-	C ₁₃ H ₂₇
23.0394	1.8744	Pentadecane	C ₁₅ H ₃₀
23.8748	0.7085	Tridecane, 1-iodo-	C ₁₃ H ₂₇
24.8818	1.4153	1-Tridecene	C ₁₄ H ₂₈
25.0192	0.9647	Hexadecane	$C_{16}H_{34}$
26.4954	1.5408	8-Heptadecene	C ₁₇ H ₃₄
26.6042	1.7616	8-Heptadecene	C ₁₇ H ₃₄
26.7701	0.9565	1-Heptadecene	$C_{17}H_{34}$
26.9017	1.7778	Heptadecane	C ₁₇ H ₃₆
27.1077	1.3435	Heneicosane	C ₂₁ H ₄₄
27.8859	0.621	Heneicosane	C ₂₁ H ₄₄
28.5668	0.8421	1-Octadecene	C ₁₈ H ₃₆
28.687	0.6565	Octadecane	C ₁₈ H ₃₈
30.2777	0.5346	1-Heptadecene	C ₁₇ H ₃₄
30.3864	0.625	Nonadecane	C ₁₉ H ₄₀
30.455	2.5402	Hexadecanenitrile	C ₁₆ H ₃₁ N
30.8098	0.8253	Octacosane	C ₂₈ H ₅₈
30.8441	1.3848	Hexadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂
31.485	1.7717	Pentacosane	C ₂₅ H ₅₂
31.9084	0.7195	Pentafluoropropionic acid, tetradecyl ester	C ₁₇ H ₂₉ F ₅ O ₂
32.0057	0.6364	Eicosane	C ₁ /H ₂₉ 50 2 C ₂₀ H ₂₄
33.3389	2.1512	Oleanitrile	C ₂₀ H ₂₄ C ₁₈ H ₃₃ N
33.4019	2.2416	Oleanitrile	C ₁₈ H ₃₃ N C ₁₈ H ₃₃ N
33.4648	1.0301	1-Nonadecene	C ₁₉ H ₃₈
		trans-13-Octa decenoic a cid, methyl ester	
33.6136	0.9265		C ₁₉ H ₃₆ O ₂
33.7051	3.2845	Heptadecane nitrile	C ₁₇ H ₃₃ N
34.1514	0.506	Pentadecane	C ₁₅ H ₃₂
34.9639	0.4247	1-Docosene	C ₂₂ H ₄₄
	(a = =:		
35.4847	1.9255	Retene	C ₁₈ H ₁₈
	1.9255 0.4239 1.5484	Retene 1-Nonadecene Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	$\begin{array}{c} C_{18}H_{18} \\ \hline C_{19}H_{38} \\ \hline C_{23}H_{32}O_2 \end{array}$

Table 7. GC-Mass composition of the major compounds in bio-oils Jatropha seed with catalyst

R. Time	Area %	Name of compound	Molecular formula
10.7313	1.4707	Decane	$C_{10}H_{22}$
12.3049	0.5499	Naphthalene, decahydro-	$C_{12}H_{22}$
12.4479	3.3092	Decane, 4-ethyl-	$C_{12}H_{25}$
12.6024	0.786	Decane, 4-ethyl-	$C_{12}H_{25}$
13.6381	1.4026	Undecane	C ₁₁ H ₂₄
13.7067	1.0855	Undecane, 4,7-dimethyl-	C ₁₃ H ₂₈
15.2002	1.3346	Benzene, pentyl-	$C_{11}H_{16}$
15.6579	0.9901	Phenol, 4-ethyl-	C ₈ H ₁₀ O
15.8983	0.7953	1H-Indene, 1-methylene-	C ₁₀ H ₈
16.0699	0.5972	1-Dodecene	$C_{12}H_{24}$
16.2759	1.1232	Dodecane	C ₁₂ H ₂₆
18.2328	1.5482	Tetradecane	C ₁₄ H ₃₀
18.5018	0.6245	1-Tridecene	C ₁₃ H ₂₆
18.6906	0.4657	Tridecane	C ₁₃ H ₂₈
19.0224	0.643	Naphthalene, 1-methyl-	C ₁₁ H ₁₀
19.2971	0.5671	Heptadecane, 2,6,10,15-tetramethyl-	C ₂₁ H ₄₄
19.9208	0.4029	Triacetin	C ₉ H ₁₄ O ₆
20.7619	1.5538	2-Tetradecene, (E)-	C ₁₄ H ₂₈
20.9336	1.0311	Tetradecane	C ₁₄ H ₂₈ C ₁₄ H ₃₀
22.879	1.276	1-Pentadecene	$C_{15}H_{30}$
22.9649	0.988	Octadecane	C ₁₈ H ₃₈
23.0336 24.5041	2.182	Pentadecane Cyclododecene	C 15H32
24.5956		,	C ₁₂ H ₂₄
	0.8735	1,13-Tetra decadiene	C ₁₄ H ₂₆
24.876	1.4327	1-Nona decene	C ₁₉ H ₃₈
25.0191	<u>1.067</u> 2.3098	Hexadecane	C ₁₆ H ₃₄
26.4953		8-Heptadecene	C ₁₇ H ₃₄
26.6041	2.4723	3-Heptadecene, (Z)-	C ₁₇ H ₃₄
26.77	0.747	1-Heptadecene	C ₁₇ H ₃₄
26.9016	2.1115	Heptadecane	C ₁₇ H ₃₆
27.1076	1.2196	Hentriacontane	C ₃₁ H ₆₄
28.5667	0.6791	5-Octadecene, (E)-	C ₁₈ H ₃₆
28.6811	0.5977	Octadecane	C ₁₈ H ₃₈
30.3805	0.4618	Nonadecane	C ₁₉ H ₄₀
30.455	4.4447	Pentadecanenitrile	C ₁₅ H ₂₉ N
30.8383	2.8924	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$
31.4792	6.2059	n-Hexadecanoic acid	$C_{16}H_{31}O_2$
32.0056	0.5491	Eicosane	C ₂₀ H ₄₂
33.3388	4.5592	Oleanitrile	C ₁₈ H ₃₃ N
33.4018	4.9365	Oleanitrile	C ₁₈ H ₃₃ N
33.6135	2.154	7-Octadecenoic acid, methyl ester	C ₁₉ H ₃₆ O ₂
33.705	5.3974	Heptadecanenitrile	$C_{17}H_{33}N$
33.9969	1.0477	Methyl stearate	C ₁₉ H ₃₈ O ₂
34.1513	1.6609	Dodecane	$C_{12}H_{26}$
34.2315	4.6969	9-Octadecenoic acid, (E)-	C ₂₀ H ₃₈ O ₂
34.3058	4.284	9-Octadecenoic acid, (E)-	C ₂₀ H ₃₈ O ₂
34.5519	2.0914	Octadecanoic acid	$C_{18}H_{36}O_2$
35.4845	0.8868	Retene	C ₁₈ H ₁₈
35.8164	0.5276	8-Heptadecene	C ₁₇ H ₃₄
38.2311	1.0214	Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	C ₂₃ H ₃₂ O ₂
39.8561	0.4899	Diisooctyl phthalate	C ₂₄ H ₃₈ O ₄

Table 8. GC-Mass composition of the major compounds in bio-oils Jatropha seed without CaO catalyst

Different types of compounds such as normal alkanes, alkenes, saturated fatty acids and their derivatives such as esters and nitriles were identified. All the compounds were classified with an increase in retention time. Figure 8-9 shows the GC-MS images of Jatropha seed pyrolytic oil with and without using CaO catalyst.

Identified Jatropha non-catalytic oil consists of both saturated and unsaturated fatty acids. Among these, n-hexadecanoic acid, octadecanoic acid, 9-octadecenoic acid, and (E)- pentafluoropropionic acid were found to be in the highest proportions about (24%) of the total compounds while the number of phenol compounds was (2% wt.). By using nano CaO catalyst in a portion of 1%wt, the level of phenols was reduced to (1.5%wt.) and the acids eliminated and reduced to (4.5% wt.), while the formation of toluene, cyclopentanones, hydrocarbons, and several light compounds was increased as demonstrated in Table 8. and Table 9. Approximately 60% (on a mass basis) of the diesel fuel compounds have been identified ^[18-20]. Among the identified fractions, n-alkanes, branched alkanes, saturated cycloalkanes, alkylbenzenes.



Figure 6. FTIR spectrum of Jatropha seed bio-oil without using CaO catalyst.



Figure 7. FTIR spectrum of Jatropha seed bio-oil with using Nano CaO catalyst



Figure. 8. Spectrum of GC of Jatropha seed pyrolytic oil with catalyst



Figure. 9. Spectrum of GC of Jatropha seed pyrolytic oil without CaO catalyst

3.4. Jatropha charcoal (solid pyrolytic residues)

Ultimate and proximate analysis of Jatropha seed pyrolytic coal was done to find the elemental composition of bio-coal and compared it with conventional coal in Table 9.

Element	Unit	Jatropha seed char coal	Conventional coal (bitu- minous) ^[19]			
Ultimate analysis						
С	%wt.	66.85	65-80			
Н	%wt.	4.76	4.5-6			
Ν	%wt.	3.25	0.5-2.5			
S	%wt.	Nil	0.5-6			
0	%wt.	25.14	4.5 -10			
H/C molar ratio	-	14.04				
		Proximate analysis				
Moisture content	%	2.2	2-15			
Volatile matter	%	80.9	15-45			
Fixed carbon	%	8.1	50-70			
Ash	%	6	4-15			
GCV	MJ/kg	27.59	26.45			

T . I. I. O III	1 · · · · · · · · · · · · · · · · · · ·			C 3		
Table 9. U	timate and	proximate	analysis c	of Jatropha	seed pyrolytic oi	L

4. Conclusions and recommendations

The fast pyrolysis Jatropha seeds were done in a fixed bed reactor under different temperature ranges from 400 – 550°C without and with Nano CaO catalyst synthesis from the eggshell. The maximum bio-oil yield was 40% at an optimum temperature of 500°C for Jatropha kernels (seeds and shells), and with a catalyst that has a concentration of 1%wt, it reached 50%. It is very significant from the process that as the pyrolysis temperature increased, the amount of liquid product also increased up to a certain value (optimum temperature) and then it decreased because of the formation of excessive gaseous products. The SEM, EDX and XRD analysis of the catalyst showed a good agreement with literature. While FTIR analysis and GC-MS analysis showed that the bio-oils contain about 60 chemical compounds contain a large number of fatty acids, oxygen and nitrogen-bearing groups (carboxylic and amines). On the other hand, using CaO nanocatalyst (1%wt.) in this process, the level of phenols was reduced from 2 to 1.5 %wt. and the acids reduced from 24 to 4.5 %wt. While the formation of toluene, cyclopentanones, hydrocarbons and several light compounds was increased.

Different concentrations of catalyst and using different values of heating rates 25, 30, 35, 40°C are recommended.

References

- [1] Demirbas A. Political, economic and environmental impacts of biofuels: A review. Applied Energy, 2009; 86: 108–117.
- [2] McKendry P. Energy production from biomass (Part 2): conversion technologies. Bioresource Technology, 2002; 83(1): 47–54.
- [3] Jain AK, Sharma SK, Singh D. Reaction Kinetics of Paddy Husk Thermal Decomposition. Energy Research Center Panjab University, Panjab, India, 1996.
- [4] Acikgoz C, Onay O, and Kockar OM. Fast pyrolysis of linseed: product yields and compositions. Journal of Analytical and Applied Pyrolysis, 2004; 71(2): 417–429.
- [5] Tsai WT, Lee MK, and Chang YM. Fast pyrolysis of rice husk: product yields and compositions. Bioresource Technology, 2007; 98(1): 22–28.
- [6] Lehto J. Determination of kinetic parameters for Finnish milled peat using drop tube reactor and optical measurement techniques. Fuel, 2007; 86(12-13): 1656–1663.
- [7] Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. The effects of catalysts in biodiesel production: a review. J. Ind. Eng. Chem., 2013; 19: 14–26.
- [8] Parawira W. Biodiesel production from *Jatropha curcas*: A review. Scientific Research and Essays, 2010; 5(14): 1796-1808. Available online at <u>http://www.academicjournals.org/SRE</u>.
- [9] Badrul HM, Rahmat N, Steven S, Syarifah F, Shelly W, Agung PF. Synthesis and Characterization of Nano Calcium Oxide from Eggshell to be Catalyst of Biodiesel Waste Oil. Proceedings of the 3rd Applied Science for Technology Innovation, ASTECHNOVA 2014 International Energy Conference.
- [10] Jai PH, Wook JS, Kyu YJ, Gil KB, Mok LS Removal of heavy metals using waste eggshell, Journal of Environmental Sciences,2007; 19:1436–1441.
- [11] Pornchai T, Putkhan A, PutkhanA. Effect of Calcination Time on Physical and Chemical Properties of CaO- catalyst Derived from Industrial-eggshell Wastes. J Sci Technol MSU, 2016; 35(6): 693-697
- [12] Bridgwater AV. Biomass Fast Pyrolysis. Thermal Science, 2004; 8(2): 2149
- [13] Yaman S. Pyrolysis of biomass to produce fuels and chemical feedstocks. Energy Conversion and Management, 2004; 45(5): 651–671.
- [14] Sensöz S, Angin D. Pyrolysis of safflower (Charthamus tinctorius L.) Seed press cake: Part 1. The effects of pyrolysis parameters on the product yields. Bioresour. Technol., 2008; 99(13):5492-7.
- [15] Putun AE, Ozbay N, and Putun E. Bio-oil production from rapid pyrolysis of cottonseed cake: product yields and compositions. International Journal of Energy Research, Int. J. Energy Res. 2006; 30: 501–510.
- [16] Putun AE, Ozbay N, Varol EA, Uzun BB., and Ates F. Rapid and slow pyrolysis of pistachio shell: Effect of pyrolysis conditions on the product yields and characterization of the liquid product. Int. J. Energy Res., 2007; 31: 506–514.
- [17] Munir S, Daood SS, Nimmo W, Cunliffe AM, and Gibbs BM. Thermal analysis and devolatilization kinetics of cotton stalk, sugar cane bagasse and shea meal under nitrogen and air atmospheres. Bioresource Technology, 2009; 100(3): 1413- 1418.
- [18] Das P, Dinda M, Gosai N, Maiti S. High Energy Density Bio-oil via Slow Pyrolysis of Jatropha curcas Shells. Energy & Fuels, 2015; 29(7): 4311-4320.
- [19] Liang F, Lu M, Keener T, Liu Z, Khang S-J. The organic composition of diesel particulate matter, diesel fuel and engine oil of a non-road diesel generator. J. Environ. Monit., 2005, 7, 983–988
- [20] (ASTM D-3172; ASTM D3173; ASTM D-3174; ASTM D-3175; ASTM D5142; ISO 562).

To whom correspondence should be addressed: Shaimaa Saeed, Department of Chemical Engineering, Elminia University, Minia, Egypt, E-mail <u>engshaimaa24@gmail.com</u>