Modification of a Fixed Bed Reactor System for Pyrolytic Conversion of Royal Poinciana Pods into Alternative Fuels

Helen Oluwatosin Olagbende*, Elizabeth Funmilayo Aransiola*,
Babatunde Sunday Ogunsina**, Olayinka Sanda* and Oluwadamilola Oyinlola Shonibare*

*Department of Chemical Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria.

**Department of Agricultural and Environmental Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria.

(tosinhelen94@gmail.com; aransilolaef@gmai.com; bsogunsina@yahoo.com; sanchemieO2@gmail.com; damilola.shonibare@yahoo.com)

**Corresponding Author: Babatunde Sunday Ogunsina; +2348059881048; bsogunsina@yahoo.com

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Abstract - An existing fixed bed pyrolytic reactor was modified, constructed and tested. Dry and matured royal poinciana (*Delonix regia*) pods obtained from Obafemi Awolowo University campus in Ile-Ife were shelled manually to obtain the husk and seed fractions. Some physicochemical properties and proximate composition of the pods and seeds were investigated following standard procedures. *Delonix regia* pods and seeds samples were pyrolysed considering five temperature levels (300 - 500 ºC at 50 ºC interval, each lasting 7 h). The reactor utilizes a 3 kW electrical heating source to decompose bio-material subject to different temperatures. The system is fitted with a condenser for cooling and to maximize bio-oil recovery. The alternative fuel products (char and bio-oil) obtained were analysed for yield, ultimate and chemical composition using gas chromatography – mass spectrometry. The yield of bio-oil derived from the seed was found to be relatively higher than that of the pod and husk; however, all samples produced significant amount of char. The chief chemical constituents in the bio-oil were carboxylic acids, amines, amides, pyridines and phenols. This study show that *Delonix regia* tree, which hitherto, was grown merely as an ornamental plant, can be explored for alternative fuels production.

Keywords: Pyrolysis, Modification, *Delonix regia*; Pods, Alternative fuels

1. Introduction

Energy has been a subject of critical concern to man since creation. The complexities of the human society and activities related to livelihood have eaten deep into the world’s energy resources; depleting most of its valuable reserves and threatening existence. It has been widely documented that the production and use of fossil fuels is largely responsible for the menace of environmental pollution globally [1]. The world therefore, is now at an extremely critical stage in the search for alternative energy sources. This in addition to the negative impact of climate change and green house gas emissions on the environment have made research into clean, non-toxic and renewable energy a necessity in modern world.

From pre-historic times, man always depended on biomass materials such as wood, grasses, plant residues and wastes to generate energy. As compared to fossil fuels, thermo-chemical conversion of these biomass materials into alternative fuels emits less amount of CO_2 and has very negligible effect on the environment [2]. The process, which involves thermal decomposition of organic matter by pyrolysis, combustion, gasification or other methods to produce fuel may be described by the equation below [3, 4].

$$\underbrace{(C_6H_{12}O_6)_m}_{\textbf{Bio-material}}\rightarrow\underbrace{(H_2+CO+CH_4+\ldots+C_5H_{12})}_{\textbf{Gases}}+\underbrace{(H_2O+\ldots+CH_3OH+CH_3COOH+..)}_{\textbf{Liquid product}}+\underbrace{C}_{\textbf{Char}} \quad (1)$$

The main chemical components of biomass such as cellulose, hemicellulose and lignin decompose as temperature increases during pyrolysis. Moisture evaporates at about 110 ºC; hemicellulose decomposes between 200 and 260 ºC; cellulose, between 240 and 340 ºC and lignin, from 280 - 500 ºC. By the time the process attains 500 ºC, pyrolysis is usually near completion [5]. Younes and Mohammed [6] reported that a typical pyrolytic conversion process occurs in three stages based on thermo-gravimetry analysis. There is pre-pyrolysis, which occurs between 120 and 200 ºC characterized by weight reduction when some internal rearrangements, such as bond breakage, appearance of free radicals and formation of carbonyl groups take place. In the process, there is a corresponding release of small amounts of water, CO and CO_2. The second stage is the actual pyrolysis;

a process during which solid decomposition occurs and is accompanied by significant loss in the weight of the biomass. The last stage is the devolatization of char which is caused by the further cleavage of C-H and C-O bonds. The entire process brings about significant reduction in bulk, eliminates odorous emission from biodegradable wastes and ultimately, yields char and bio-oil which when fractionated gives bio-fuels [7].

Bio-fuels are fast gaining relevance in the global quest for renewable and clean energy especially because it reduces greenhouse gas emissions [8]. The feedstock for bio-fuels production largely includes biomass, grains, underutilized oil seeds, municipal and agro-industrial wastes. Some oil seeds which have been studied as materials for bio-fuels production include castor [9], *davdaru* [10], neem [11, 12], tamarind [13], sesame seed [14], *Jatropha curcas* [15, 16, 17, 18] and soybean [19, 20]. Such plant residues include jute dust [21, spent palm fruit bunches [22], peanut shell [23], cashew nut shell [24], corn cob [25. 26], almond shell [27] and hazelnut shell [28]. Similar reports were found on sawdust [3], apple pulp [29], sugarcane bagasse [30] and palm kernel wastes [31].

Royal poinciana (*Delonix regia)* tree is well known for its brilliant flowers as an ornamental plant in the tropics (Fig. 1). Being a deciduous tree with broad canopy, it is also a source of shade wherever it blossoms. The brightly coloured flowers mature into tender green pods which turns dark brown at maturity. The pods which remain on the tree for many months and fall off towards the end of its fruiting season constitute serious waste, the disposal of which is a menace in parks and gardens. Despite the enormous quantity of *Delonix regia* pods produced in the tropical coast of West Africa during the dry season, it is rarely known for any food, industrial or medicinal application; hence, it was conceived that a widely available biomass of this nature may be explored as a feedstock for thermochemical conversion into alternative fuels.

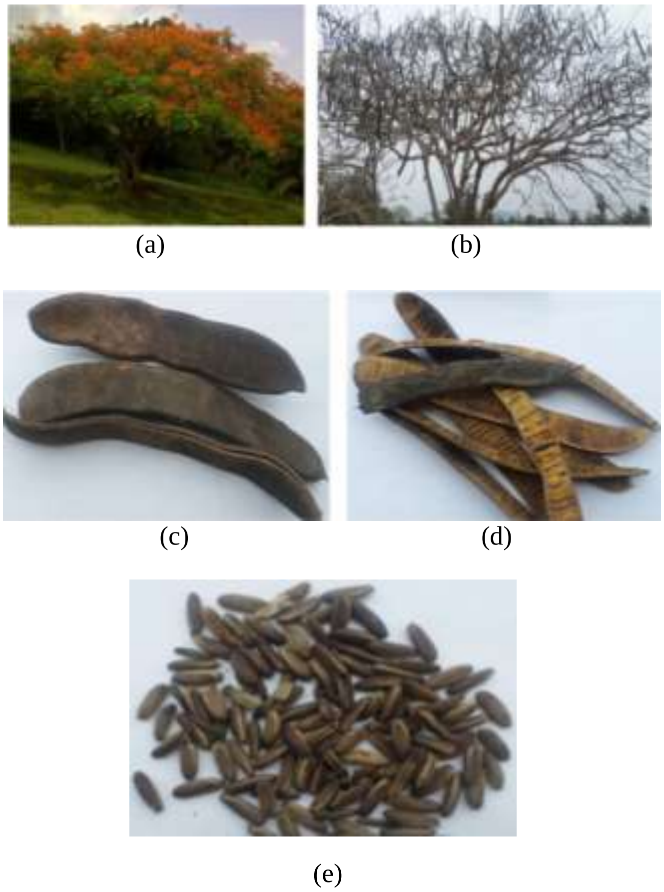

(a) (b)
(c) (d)
(e)

Fig. 1. *Delonix regia* tree and its products

a) *Delonix regia* tree during its flowering season in Ile Ife, Nigeria. b) *Delonix regia* tree during its fruiting season
c) A collection of *Delonix regia* pods; d) husks and e) seeds

Our research group has previously investigated the pyrolytic conversion of municipal solid wastes, spent palm fruit bunches, cashew nut shells and corn cobs into alternative fuels using a locally developed fixed bed reactor system [15, 22, 24, 26]. In this study, the existing reactor design (Fig. 2) was modified to convert *Delonix regia* pods, seeds and husks into alternative fuels. The process was analysed for yield and the products were characterized.

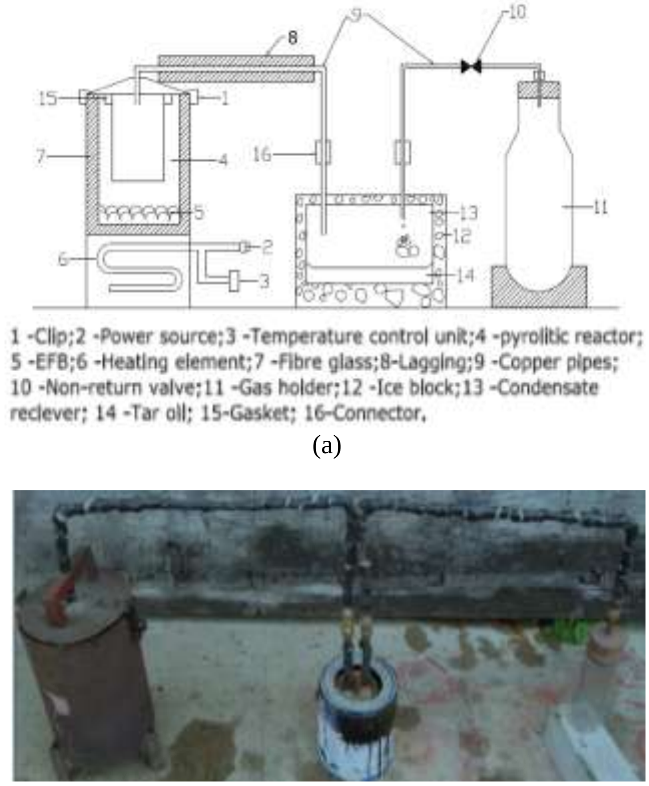
2. Methodology

2.1 Limitations and Modifications of the Existing Reactor

The limitations of the existing design include slow rate of heat transfer within the reactor chamber from the heating chamber to the feedstock. Furthermore, the use of ice bed to cool hot gaseous products from the reactor is slow and inefficient for maximum liquid recovery as it results in incomplete condensation. In view of the above limitations, a modified reactor design was conceived and developed considering size of the reactor, operating temperature, rate of heat transfer and physical properties of the feedstock and products. Design criteria include:

i) Short vapor residence time in the reactor;
ii) Rapid condensation of the vapor product to promote high yield of liquid product;
iii) Sufficient heat supply to the system;
iv) Rapid and uniform heat-transfer within the reactor so that less energy is consumed. hence, conserving energy, and
v) Adequate vapor and water mass flow rate ratio for effective condensation.

The heat source was a 3 kW heating element built to pass through the centre of the biomass in the reactor chamber. This ensures uniform heat transfer across the reactor. A tubular heat exchanger was introduced for efficient cooling during the entire process. The shell is made of mild steel and the tube (0.635 cm diameter) of length 2.5 m is made of copper. The condenser was tilted at an angle of about 18^o alongside with the condensate conveyor pipe in order to eliminate bio-oil hold-up within the system.



(a)

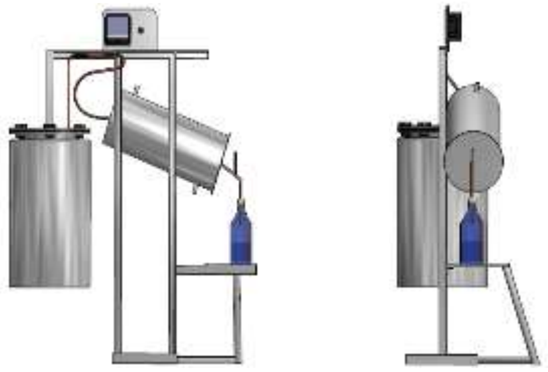
(b)

Fig. 2.
(a) Schematic diagram of existing pyrolytic reactor system
(b) Pictorial view of existing pyrolytic reactor system [22]

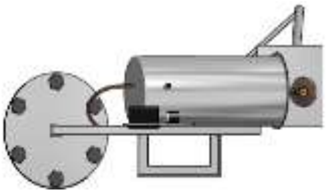
The modified fixed bed pyrolytic reactor was conceived as a cylindrical device for batch process to prevent the entire surface from wobbling and large amplitude vibration. The dimensions of the modified reactor were 0.25, 0.5 m and 25.2 m^3 for diameter, height and volume respectively. The configuration is such that fluid flow through the bed is parallel to the axis of the cylinder. The inner tube was a copper pipe of length 2.5 m and 6.35 mm (0.25 inch) diameter, wound like a coil and encased by a mild steel shell. The length and diameter of the modified condenser are 0.47 × 0.19 m, respectively. The diameter of the copper pipes linking the reactor to the condenser unit is 10 mm and 6 mm for the pipe connecting the condensing unit to the condensate receiver.

The condenser has a multi-pass flow arrangement and it is tilted such that the cooling fluid travels along the axis of condensate flow. The headers (larger flow areas at both ends of the shell) where designed to be adequate for fluid accumulation [32]. The design allows hot gasses to pass through the inner tube and condense as water circulates around the tube (within the shell). Heat exchange in the condenser is by convection within the fluid and by conduction through the wall separating the two fluids. The condenser was designed to maximize the surface area of the wall between the two fluids while minimizing resistance to fluid flow through the exchanger.

The orthographic drawing of the modified machine is shown in Fig. 3, while Fig. 4 shows its exploded view.



Side view Front view



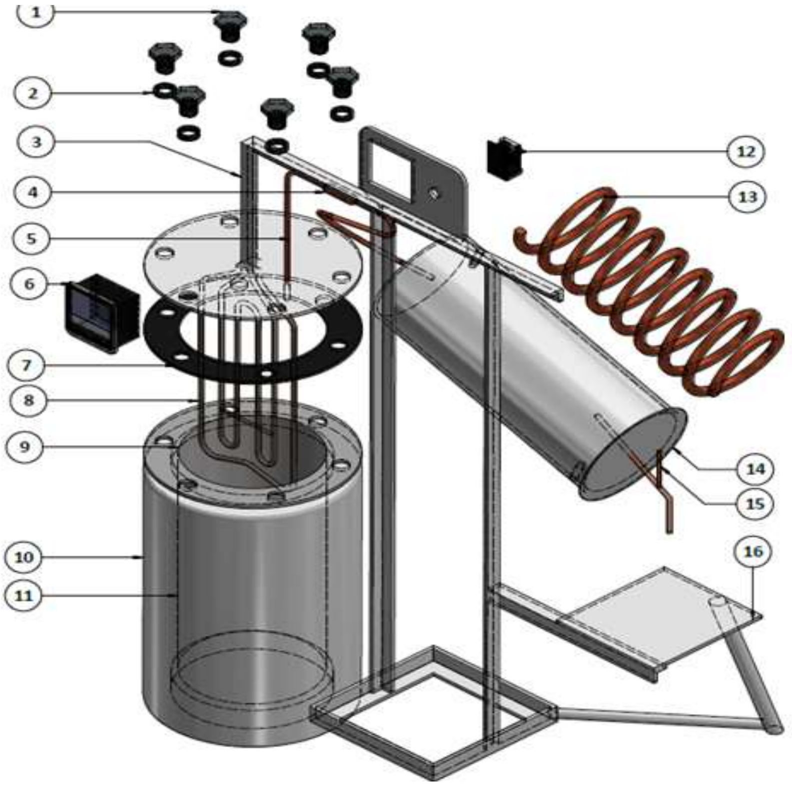
Plan view

Fig. 3. Orthographic view of the modified pyrolytic reactor system

2.2 Determination of Physico-Chemical Properties of Delonix regia Seeds and Pods

a) Hull-seed ratio (HSR) was carried out following the method of Ogunsina [33]. A pod of known weight was randomly selected and split to obtain the number and total weight of seeds it contains. The HSR was obtained as a percent ratio of the mass of pod to that of the seeds. The value reported was an average of 20 replicates.

b) Proximate components such as volatile matter, ash and fixed carbon were determined following the AOAC [34] procedure as follows:
i) Moisture content: Approximately 100 g of pods and seeds were taken in aluminum dishes of known weights using an electronic balance (Mettler PM 6000, made in Germany). Samples were oven dried at 130 °C for 6 h and afterwards weighed. The percentage moisture content was calculated by gravimetry.
ii) Volatile matter: Approximately 5 g of dried *Delonix regia* pod and seed samples was weighed into a pan and heated at 900 °C for 10 mins in the absence of air to vaporize volatile matter. The pan was weighed afterwards. The difference between the initial weight (W_I) before heat was applied and the final weight (W_F) represents the volatile matter (%) which is = $(W_I – W_F) \times 100$ (2)
iii) Ash: Dry sample of known weight was heated in a furnace at 550°C for 12 h, the greyish-white residue formed after charring and incineration of sample comprised of the total ash.



PARTS LIST			
S/N	Qty	PARTS DESCRIPTION	MATERIAL
1	6	Bolt	Steel
2	6	Nut	Steel
3	1	Frame	Mild Steel
4	1	Accumulator	Composite
5	1	Pipe	Copper
6	1	Temperature regulator	Composite
7	1	Gasket	Composite
8	1	Heating Element	Copper
9	1	Reactor	Mild steel
10	1	Reactor Jacket	Aluminium
11	1	Lagging Material	Fiber glass
12	1	Contactor	Composite
13	1	Condensing tube	Copper
14	1	Condensing shell	Mild steel
15	1	Gas outlet	Copper
16	1	Gas collection platform	Galvanized steel
PROJECT TITLE: CONVERSION OF ROYAL POINCIANA *(Delonix regia)* PODS INTO ALTERNATIVE FUELS BY PYROLYSIS			
DESIGNED BY		OGUNDAHUNSI, Olufemi E	SCALE: 1:2
CONCEPT		OLAGBENDE Oluwatosin H SHONIBARE Damilola O.	DATE: 06/008/2015
APPROVED BY		ENGR. DR. B.S. OGUNSINA & ENGR. Dr MRS. E.F. ARANSIOLA	EXPLODED VIEW

Fig. 4. Exploded view and part list of the modified pyrolysis reactor

iv) Fixed carbon: The fixed carbon composition was estimated by difference as follows:

Fixed carbon (%) = 100–(%moisture+%ash+%volatile matter) (3)

2.3 Pyrolysis of Delonix regia

Dry and matured *Delonix regia* pods obtained from parks and garden trees in Obafemi Awolowo University campus, Ile-Ife were shelled manually to obtain seeds and husks separately. The particle size of about 20 kg each of the pod, seed and husk fractions were reduced; the seeds were milled to pass through 2-3 mm mesh sieve while the pods and husks were manually broken into smaller particles. The samples were oven dried at 130˚C for 6 h. About 2 kg of each fraction of the pod, seed and husk was fed to the reactor in batches. The reactor was tightened to prevent heat loss and escape of volatile products and water kept running for condensation as the experiment progressed. The temperature controller was set to the operating temperature applicable for each experimental run; each lasting 7 h. After 7 h, the power source was turned off and the pyrolytic products were collected. The weight of char and bio-oil fraction obtained were measured, labelled, stored in clean air tight containers and moisture free environment; the bio-oil was stored in a temperature controlled environment at 16 ºC. All the parts of the reactor were cleaned and re-assembled for the next experimental run. The entire process include harvesting of dry and mature pods, drying, size reduction, weighing, pyrolysis, products collection, measurement and storage until the time of analysis. The performance of the reactorwas evaluated on the basis of its conversion efficiency and yield as documented by Fogler [35]:

$$\text{Conversion efficiency} = \left[1 - \left(\frac{\mathrm{M_C}}{\mathrm{M_f}}\right)\right] \times 100 \tag{4}$$

$$Y_c = \frac{M_c}{M_f} \times 100 \tag{5}$$

$$Y_B = \frac{M_B}{M_f} \times 100 \tag{6}$$

where: Y_C = Char yield; Y_B = Bio-oil yield; M_c= Mass of char; M_B = Mass of bio-oil; M_f = Mass of feedstock

2.4 Characterization of Pyrolytic Products

a) Gas chromatography-mass spectrometry (GC-MS): The bio-oils obtained by pyrolysis were analyzed by GC-MS (7890A, Agilent Technologies, USA) installed with a 30 m × 250 µm × 0.25 µm capillary column (Agilent-5 MS, Agilent Technologies, USA) at 300 ºC injector temperature. The temperature of the oven was programmed from 35 - 250 ºC at a heating rate of 4ºC/min. Helium (chromatographic grade) was used as the carrier gas with a 3 ml/min flow rate and the mass range of the spectrometer was set from 50 to 750. Peak identification was based on computer matching of the mass spectra with that of

Mass Spectra Library, National Institute of Standards and Technology.

b) Ultimate analysis and heating value: The carbon hydrogen-nitrogen-sulphur (CHNS) analysis of bio-oils was performed using an elemental analyzer and the heating value was calculated from the percent of carbon, hydrogen and oxygen from CHNS analyses using the modified Dulong's formula [36]:

$$\text{Heating value (MJ/kg)} = \frac{33.5\times\%C}{100} + \frac{142.3\times\%H}{100} - \frac{15.4\times\%O}{100} \quad (7)$$

c) Moisture content of the bio-oil samples was determined using the E871 procedure. Approximately 50 g of bio-oil was weighed in a pan, the weight of the pan and bio-oil was recorded. The sample was oven dried at 100 ^{o}C to constant weight.

d) Specific gravity was determined using the ASTM D1298 method. A clean dry 50 ml density bottle of known weight was filled with distilled water and subsequently with bio-oil. The weight in each case was determined and specific gravity was calculated as a ratio of mass of bio-oil to mass of water.

e) Viscosity determination was carried out according to ASTM D445 procedure. A viscometer was inserted into a water bath at a set temperature and left for 30 min. The bio-oil was placed in the viscometer and allowed to remain in the bath until the temperature was 40 ^{o}C. The sample was allowed to flow freely and the time required for the bio-oil to pass from the first to the second mark is taken using a stop watch. An average of three replicates was multiplied by the viscometer calibration to obtain kinematic viscosity.

f) Flash point: The ASTM D93 procedure for determining flash point was employed. A sample of bio-oil was heated in a close vessel and ignited. The bio-oil is placed in the cup in such quantity as to just touch the prescribed mark on the interior of the cup. The cup lid is fitted and the apparatus was heated with bunsen burner at about 5^{o}C/min. The oil was constantly stirred intermittently as heating progressed. The injector burner was lighted and injected into the oil container at 12 s interval until a distinct flash was observed within the container. The temperature at which the flash occurred was recorded; values documented were average taken.

2.5 Thermo-gravimetric Analysis

An analytical balance was modified for thermo-gravimetric analysis to study the loss of weight of feedstock as temperature increases. Such weight loss per time and temperature increase are often associated with devolatization.

3. Results and Discussion

The modified fixed bed reactor system is shown in Fig. 5.
Pyrolytic conversion of bio-materials using uniquely different reactor's designs has been widely reported. When there is adequate thermal condition for biomass decomposition followed by rapid vapor condensation, the yield and nature of pyrolytic products is almost consistent for most bio-materials; regardless of the reactor's design or size [35]. One major advantage of fixed bed reactors is their higher conversion per weight of feedstock.

By proximate analysis, the moisture content, volatile matter, ash and fixed carbon composition were found to be: 3.83, 4.24; 75.60, 51.30; and 1.41, 5.70, 19.15, 38.76%, respectively for *Delonix regia* pods and seeds respectively. Minkova *et al.* had earlier submitted that the moisture content of a pyrolysed biomass feedstock affects the rate of heat transfer and yield [37]; hence, materials with high moisture content yield high quantity of liquid fraction. Bio-materials with high volatile matter often yield high proportion of bio-oil, whereas fixed carbon increases with bio-char yield. In most cases bio-char obtained in the presence of steam behave like activated carbons.

Fig. 5. Pictorial view of the experimental pyrolytic reactor

3.1 Recovery of Pyrolytic Products and Feedstock Conversion Efficiency

The effect of temperature on feedstock conversion efficiency of the modified reactor system is shown in Fig. 6. The percentages of feedstock converted during pyrolysis were 79.99, 71.43 and 74.19% for the pod, seed and husk, respectively. The results show that feedstock conversion efficiency was above 50%; implying that *Delonix regia,* which hitherto had been a waste can be decomposed by pyrolysis and converted into alternative fuels.

In Table 1 it was observed that the volume of bio-oil obtained from the pod increased as temperature increased from 300 to 450 ^{o}C and a decrease was observed at 500 ^{o}C. The results show that char weight decreased across the entire temperature range. This suggests that at temperatures above 450 ^{o}C, secondary decomposition of bio-material occurred; thereby, increasing the recovery of gaseous products and ultimately reducing the volume of

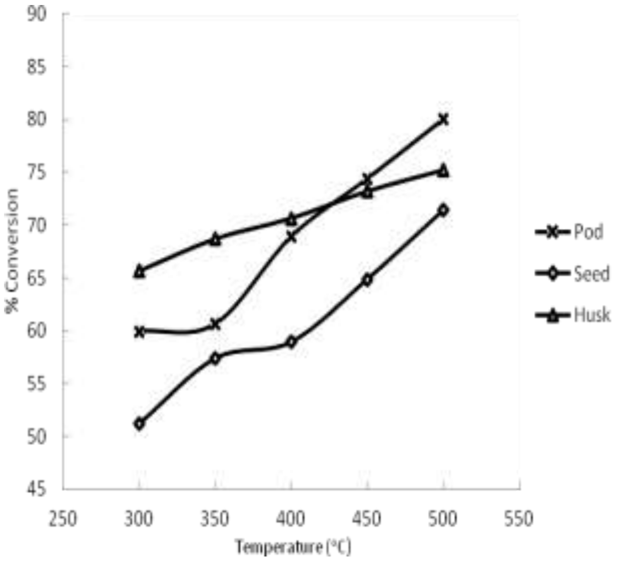


Fig. 6. Effect of temperature on feedstock conversion efficiency of the reactor

Table 1. Bio-oil and char recovery from the pyrolysis of *Delonix regia*

	Seed		Pod		Husk	
T (°C)	B (ml)	C (g)	B (ml)	C (g)	B (ml)	C(g)
300	26.6	976.7	15.2	801.3	16.8	687.6
350	28.2	852.6	29.7	787.2	36.2	626.9
400	31.3	821.5	32.6	621.8	42.6	587.6
450	34.6	702.6	38.6	512.6	28.4	536.2
500	52.6	571.4	34.1	400.2	23.1	496.3

B – Bio-oil; C – Char

bio-oil obtained. It may therefore be inferred that the optimum temperature for bio-oil recovery from *Delonix regia* pod is 450 °C. Similarly, pyrolysis of husk samples also indicate an increase in the volume of bio-oil as the operating temperature increased from 300 to 400 °C. It was observed that at 450 °C, bio-oil yield reduced drastically from 42.6 ml obtained at 400 °C to 28.4 ml; suggesting that secondary cracking of the bio-material occurs at temperatures beyond 400 °C. This is in agreement with previous finding by Oramahi *et al.* [38] that the acceptable temperature range for the pyrolysis of lignocellulosic materials for optimal bio-oil yield is between 400 and 450 °C. The weight of char obtained from the pyrolysis of *Delonix regia* pod and husk decreased with increase in operating temperature; implying that the decomposition of volatile matter increased as temperature increased. For the seed however, an increase in bio-oil yield was observed over the entire temperature range considered. The maximum and minimum bio-oil yield obtained were 52.6 ml at 500 °C and 26.6 ml at 300 °C respectively. The rate of decomposition increased as operating temperature increased, causing an increase in the volume of bio-oil produced. The low yield of bio-oil at lower temperatures may be attributed to incomplete pyrolysis occasioned by insufficient heat supply and incomplete decomposition of the feedstock. The weight of bio-char was observed to decrease as temperature increased; at 500 °C, a sharp decrease was observed. This implies that the extent of bio-material thermal decomposition increased as temperature increased; ultimately reducing char yield.

The effect of temperature on bio-oil and char yield obtained by the pyrolysis of *Delonix regia* pod, seed and husk are shown in Table 2. For the pod and husk, it was observed that bio-oil yield increased as temperature increased but decreased at 500 °C (for the pod) and 450 °C (for the husk). This may be attributed to secondary decomposition of bio-materials which usually occurs at high temperatures. Bio-oil yield for the seed was observed to increase as temperature increased. For the pod, bio-char yield was 40.07, 39.36, 31.09, 25.63 and 20.01% at 300, 350, 400, 450 and 500 °C, respectively. It was observed that bio-char yield decreased with increasing temperature; this is due to increase in extent of bio-material decomposition at higher temperature levels which results in an increase in the formation of volatile products and decrease in bio-char formation. A similar trend was observed for bio-char yield in the seed (48.84, 42.63, 41.08, 35.13 and 28.57%) and husk (34.38, 31.35, 29.38, 26.81 and 24.82%) when pyrolysed over the same temperature range indicated above. A sharp decline was observed in char yield obtained from the seed when pyrolysed at 450 °C; this may be attributed to lignin decomposition between 420 and 500 °C [39].

Table 2. Effect of temperature on bio-oil and char yield obtained by the pyrolysis of *Delonix regia* pod, seed and husk

	Yield (%)					
	Pod		Seed		Husk	
T(°C)	Bio-oil	Char	Bio-oil	Char	Bio-oil	Char
300	0.98	40.07	1.42	48. 84	0.85	34.38
350	1.73	39.36	1.49	42.63	1.76	31.35
400	1.85	31.09	1.64	41.08	2.06	29.38
450	2.14	25.63	1.77	35.13	1.39	26.81
500	1.93	20.01	2.71	28.57	1.14	24.82

3.2 Products Characterization

The viscosities of bio-oils derived from pod, seed and husk sample were 3.79×10^{-5}, 0.848×10^{-5} and $2.1 \times 10^{-5} \mathrm{m}^3/s$ respectively. Viscosity values obtained for the pod and husk are relatively higher than acceptable standard for bio-oils. Viscosity is the most important property of biofuels since it affects the operation of fuel injection equipment. As the temperature of oil is increased, its viscosity decreases and it is therefore able to flow more readily. Whereas, at low temperatures, viscosity is high and fuel atomization becomes poorer; this affects the operation of the fuel injectors significantly. The average specific gravity of the bio-oils ranges from 1.03 to 1.05 g/cm^3. This is close to the specific gravity of water, perhaps due to high proportion of water in the bio-oil fraction. The low percentage of moisture in the husk derived bio-oil is responsible for its relatively high calorific value (13.38 kJ/g) when compared to pods and seeds derived bio-oils for which calorific values were 9.12 and 4.57 kJ/g, respectively. The flash points obtained for *Delonix regia* pod, seed and husk samples are 138, 164 and 143 ^{o}C, respectively. Edward and Peggy [39] had earlier reported 197 ^{o}C for bio-diesel obtained from *Delonix regia*. Generally, the physical properties of *Delonix regia* bio-oils compare favourably with those of bio-oils obtained from other non-edible plants such as *Jatropha curcas* [41], palm oil [42] and soybean oil [43].

The components identified by GC-MS spectra for *Delonix regia* pod, seed and husk samples are shown in Table 3, 4 and 5, respectively. From the GC-MS, carboxylic acids, phenols, pyridines, furans, amines and amides were the chief chemical groups present in the bio-oils. Most of the compounds identified in the bio-oils originate from the thermal cracking of cellulose, hemicellulose and lignin in the bio-material [44]. Carboxylic groups comprising of 4-hydoxy-3-methoxy-benzoic acid, 3-Hydroxy-4-methoxybenzoic acid and 3-cyclopentyl propionic acid are formed from the pyrolysis of hemicelluloses; whereas, phenols originate from pyrolysis of lignin [44]. *Delonix regia* husk derived bio-oil contains significant amount of phenolic derivatives including 3-methyl phenol; 2, 6-dimethoxyphenol; 4-ethoxymethyl-2-methoxy phenol; 1-(4-methylthiophenyl)-2-propanone; 3,5-bis(1,1-dimethylethyl) phenol and 2-tert-butyl thiophenol which could be due to higher amount of lignin in the husk compared to pod and seed [45. 46]. Some of the derivatives from lignin found in the bio-oil samples are 1,4-benzenediol, 2-cyclopenten-1-one and 2-propanone. Phenol is the most abundant phenolic compound present in *Delonix regia* pod bio-oil sample, which is responsible for its higher carbon and hydrogen fractions and calorific value when compared to bio-oil derived from *Delonix regia* seed. The derivatives of cellulose and hemicellulose found in the bio-oils include 2-furanmethanol, 2,4-dimethylfuran, 2,5-dimethyl-furan and 3-methyl-furan. Pyridine and pyridine derivatives such as 2-methyl-pyridine, 2,3-dimethylpyridine, 2,6-dimethylpyridine, 2,4-dimethylpyridine and 3-methylpyridine were abundant as a result of thermal cracking.

The results of ultimate analysis and heating value of bio-oils obtained from *Delonix regia* pod, seed and husk samples are presented in Table 6. Carbon content was higher in husk derived bio-oils than that of pod and seed

Table 3. GC-MS spectra for *Delonix regia* pod derived bio-oil

Peak	RT (min)	Library/ ID	% Area
1	8.096	Hydrazine, 1,2-dimethyl	22.70
2	10.000	Ethanamine, N,N-dimethyl	8.37
3	14.333	2,4-Dimethylfuran	6.75
4	19.250	3,4-Methylpropyl Succinimide	31.90
5	20.915	Cyclohexylamine, N-ethyl-	9.74
6	38.480	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)	11.93
7	39.069	Pyrrolo (1,2-a) pyrazine-1,4-dione,hexahydro	4.32
8	40.271	4-Oxoadamantane-1-carboxylic acid	2.55
9	40.624	1-Oxa-3-azaspiro[4.5] decane-3-acetamide, N-(4-fluorophenyl) – 4-hydroxyl	1.73

Table 4. GC-MS spectra for *Delonix regia* seed

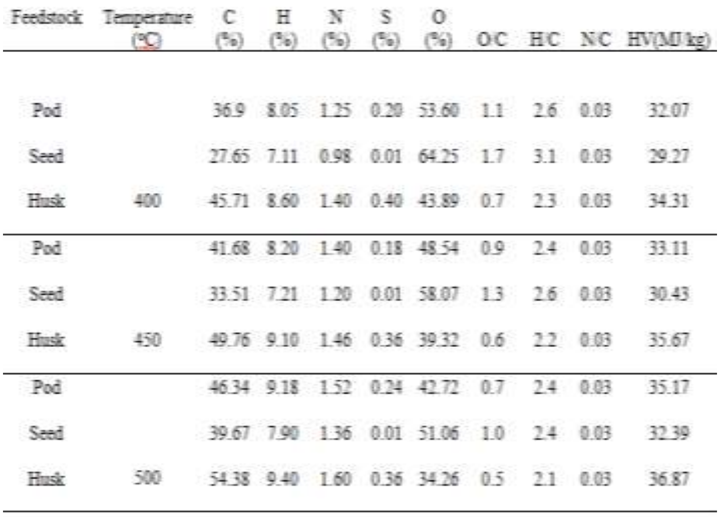
Peak	RT	Library/ ID	% Area
1	9.729	Hydrazine, 1,1-dimethyl	46.94
2	31.276	Benzoic acid, 4-hydoxy-3-methoxy	14.07
3	33.633	Ethanone, 1-(2,6-dihyroxy-4-methoxyphenyl)	11.34
4	33.932	2-propanone, 1-(4-hydroxy-3-methoxyphenyl)	6.40
5	38.480	Ethanone, 1- (4-hydroxy-3,5-dimethoxyphenyl)	2.52
6	38.857	3,5 –Dimethoxy – 4 – hydroxyphenulacetic acid	5.52
7	39.367	2,5-Diethoxyaniline	1.85
8	39.925	2-Cylohexen-1-one, 2-methyl-5-(1-methylethenyl)-O-methyloxime)	7.33
9	40.624	Diphenamide	4.03

Table 5. GC-MS spectra for *Delonix regia* husk

Peak	RT	Library ID	% Area
1	7.098	2-Tetradecanone	1.51
2	8.174	Hydrazine, 1,1-dimethyl-	1.19
3	8.630	Pyridine	7.62
4	9.266	Pyridine, 2-methyl-	0.86
5	10.201	Pyridine, 2-methyl-	3.81
6	10.774	2-Furanmethanol	0.90
7	11.253	2-Furanmethanol	4.64
8	11.379	Pyridine, 3-methyl-	1.22
9	11.458	Pyridine, 4-methyl-	1.21
10	11.945	Pyridine, 2,3-dimethyl-	0.62
11	12.518	Pyridine, 2-ethyl-	0.74
12	12.974	2-Piperidinemethanol	3.28
13	13.586	Pyridine, 2,3-dimethyl-	2.99
14	13.948	Pyridine, 2,6-dimethyl-	0.96
15	14.403	2-Cyclopenten-1one, 3-methyl-	2.99
16	14.757	Phenol	0.97
17	15.802	Bicyclo[2.2.1]heptane-2carboxalde	6.98
18	16.430	Phenol	11.58
19	18.29	Phenol, 3-methyl-	1.95
20	19.564	p-Cresol	2.86
21	20.161	Maltol	1.20
22	20.444	2-Cyclopenten-1one, 3-ethyl-2-hydoxy	2.17
23	21.230	4, 5-Diamino-2-hydroxypyrimidine	0.97
24	21.583	1-Piperidinepropanenitrile	0.56
25	22.683	1,4-Benzenediol, 2, 6 – dimethyl-	3.45
26	28.323	Phenol, 2, 6- dimethoxy-	14.92
27	31.284	3-Hydroxy-4-methoxybenzoic acid	4.58
28	32.746	2-tert-Butylthiophenol	0.73
29	33.350	Phenol, 3,5-bis(1,1-dimethylethyl)	1.07
30	33.649	Hydoquinone mono-trimethylsilyle	2.20
31	33.971	1- (4-methylthiophenyl)- 2-propanone	2.62
32	37.372	Phenol, 4-(ethoxymethyl)-2-methoxy	0.52
33	38.503	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)	1.56
34	38.881	1-Butanone, 1-(2,4,6-trihydoxy-3-methylphenyl)-	2.74
35	39.383	2-Azafluorenone	0.62
36	39.941	2-Methoxybenyl alcohol	1.21

derived bio-oils. The higher carbon and hydrogen content in pod and husk derived bio-oils signify a higher degree of cross-linking and occurrence of higher molecular weight components compared to seed derived bio-oils. The carbon and hydrogen content compares favourably with 45.7, 7; 51.6, 6.3 and 48.5, 5.5% obtained for pine, wood and wheat straw, respectively [47]. The oxygen content is close in value to 49, 47, 41.5 and 49.13% reported for birch, pine, wood and switch grass, respectively. The atomic ratios (H/C, O/C, N/C and S/C) for the bio-oils were calculated to obtain their empirical formulae. The empirical formula for pod, seed and husk derived bio-oils at 400 ºC are $CH_{2.6}N_{0.03}O_{1.1}$, $CH_{3.1}N_{0.03}O_{1.7}$ and $CH_{2.3}N_{0.03}O_{0.7}$, respectively. Similarly, the empirical formula for pod, seed and husk derived bio-oil at 500 ºC are $CH_{2.4}N_{0.03}O_{0.7}$, $CH_{2.4}N_{0.03}O_{1.0}$ and $CH_{2.1}N_{0.03}O_{0.5}$ respectively. The heating value of husk derived bio-oils (34.31 - 36.87 MJ/kg) was found to be higher than that of pod (32.07 - 35.17 MJ/kg) and seed (29.27 - 32.39 MJ/kg) derived bio-oils. The higher heating values, carbon and hydrogen contents coupled with low oxygen contents in the husk derived bio-oils suggest that they are better in terms fuel properties than pod and seed derived bio-oils. Pod derived bio-oils had relatively higher heating value than seed derived bio-oils at all temperatures due to their higher carbon and hydrogen content.

Table 6. Ultimate analysis and heating value of *Delonix regia* bio-oil samples



Feedstock	Temperature (ºC)	C (%)	H (%)	N (%)	S (%)	O (%)	O/C	H/C	N/C	HV(MJ/kg)
Pod		36.9	8.05	1.25	0.20	53.60	1.1	2.6	0.03	32.07
Seed		27.65	7.11	0.98	0.01	64.25	1.7	3.1	0.03	29.27
Husk	400	45.71	8.60	1.40	0.40	43.89	0.7	2.3	0.03	34.31
Pod		41.68	8.20	1.40	0.18	48.54	0.9	2.4	0.03	33.11
Seed		33.51	7.21	1.20	0.01	58.07	1.3	2.6	0.03	30.43
Husk	450	49.76	9.10	1.46	0.36	39.32	0.6	2.2	0.03	35.67
Pod		46.34	9.18	1.52	0.24	42.72	0.7	2.4	0.03	35.17
Seed		39.67	7.90	1.36	0.01	51.06	1.0	2.4	0.03	32.39
Husk	500	54.38	9.40	1.60	0.36	34.26	0.5	2.1	0.03	36.87

Carbon, C; Hydrogen, H; Nitrogen, N; Sulphur, S; Oxygen, O and Heating Value, HV

Figure 7 shows the devolatization characteristics for *Delonix regia* pod, seed and husk. The trend shows that all biomass began to devolatilize at a temperature between 220 and 250 ºC. Weight loss continued until about 380 ºC, owing to loss of moisture, volatile compounds and organic components including cellulose, hemicellulose and lignin [35]. This phase was followed by a steady and slower weight loss phase that started between 400 and 450 ºC and continued up to 500 ºC, indicating char formation.

Hemicellulose is known to degrade at a temperature range of 200 - 300 ^oC, cellulose at 25 - 350 ^oC and lignin at a wider range of 200 - 500 ^oC [38].

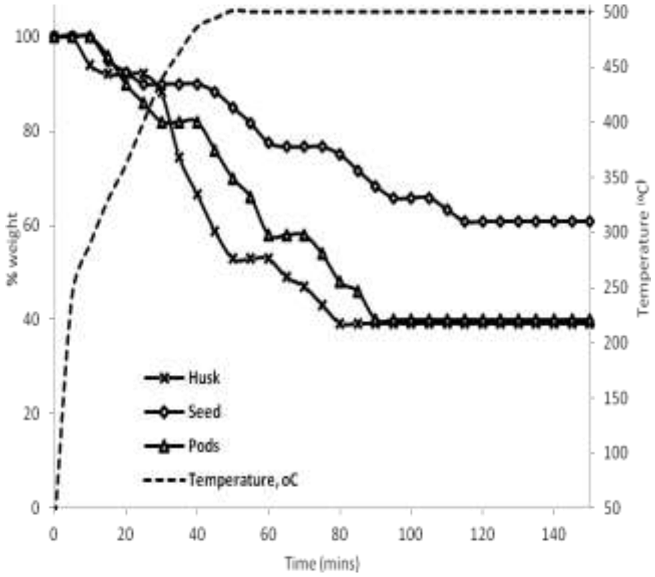


Fig. 7. Thermogravimetric analysis of *Delonix regia*

2. Conclusions

Thermochemical conversion of *Delonix regia* into alternative fuel products was undertaken using a locally built modified fixed bed reactor system which was operated at temperatures ranging between 300 - 500 °C. The proximate composition of *Delonix regia* shows 75.6 and 51.3% of volatile matter for pod and seed, respectively. The maximum bio-oil and bio-char yield obtained from *Delonix regia* seed were 2.71% at 500 °C and 48.84% at 300 °C, respectively. The calorific values of the bio-oils were: 9.16, 13.38 and 4.57 kJ/kg for the pod, seed and husk; while the corresponding values for bio-char were: 14.66, 14.54 and 14.03 kJ/kg, respectively. *Delonix regia* derived bio-oils notably contain carboxylic acids, phenols, pyridines, amides and amines. A rarely reported chemical such as pyridine which was found in the bio-oils is a valuable material for the agro-chemical and pharmaceutical industries. The utilization of *Delonix regia* pods as a feedstock for alternative fuels abates the menace that its disposal constitutes. A material such as this, if properly explored may be of great value to the bio-fuel industry.

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