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Rapid And Catalytic Pyrolysis Of *Eriobotrya Japonica* Seed Oil: Effect Of Temperature And Catalyst Additives

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ABSTRACT

Pyrolysis of *Eriobotrya japonica* seed oil was investigated in steel-made fixed bed reactor with (Alumina, Red mud, and Bentonite clay) and without catalyst at three different temperatures. The influence of pyrolysis parameters such as catalyst and temperature on the percentage yield was studied. It was found that temperature, as well as catalyst, affect the percentage yield of pyrolytic products. Results indicate that yield of bio-oil was significantly improved while using red mud and bentonite clay but remarkable results were obtained with alumina due to the presence of acidic sites. However, it was further observed that at 550°C the aromatic content increased considerably with alumina. Additionally, bio-oil obtained at different temperatures (350°C and 550°C) was investigated by elemental analysis and GC-MS, and about 44 and 53 different compounds were identified in liquid products.

Keywords: Biomass; Bio-oil; Biofuel; Energy; Pyrolysis

Introduction

Global warming resulted in excessive flooding, frequent wildfires, and severe droughts (Lizundia-Loiola, Pettinari, & Chuvieco, 2020). To fulfill the need for energy, the consumption of fossil fuels is increasing daily (Yu, Xu, Abramson, Li, & Guo, 2020). Due to the rise in the usage of fossil fuels by industrial mutiny, 1.83 trillion tons of CO_2 emissions have been observed (Allen et al., 2009). As a result of this excessive use of fossil fuel, the fine particulate matter (SO_x and NO_x) is increasing in the atmosphere and resulting in the greenhouse effect and global warming. Further, it is also not possible to stop using the consumption of fossil fuels as the energy sectors, all over the world, mostly depend on them (Hoffert et al., 1998). Thus, to eliminate these environmental problems, the use of renewable energy is gaining importance nowadays. It is reported that the sources required for renewable energy are biomasses, which may be plants or plant-derived materials (Allen et al., 2009). The annual production of biomass is about a hundred billion tons which can be used to generate heat, electricity, and chemicals. Different techniques like fermentation, liquefaction, gasification, and pyrolysis are reported for the conversion of biomass into bio oil (Atanda et al., 2020; Perkins, Bhaskar, & Konarova, 2018). The present research is focused on the pyrolysis of biomasses. It is reported that bio char and bio oil are produced during the pyrolysis of biomass (named as feedstock) in the absence of oxygen between temperatures ranging from 350 to 650 ^{o}C (Foong et al., 2020; Krutof & Hawboldt, 2018).

Reported research revealed that biomass catalytic pyrolysis can be done with and without a catalyst. The palm kernel cake pyrolysis and jatropha seed shell cake pyrolysis at a temperature of 400 - 500 ^{o}C confirmed the yield of 48 wt. % of jatropha seed cake shell. Elemental analysis of its Bio oil showed the presence of H (6.15%), N (2.32%), C (50.52%), and O (39.41%) with 20.80 MJ/kg heating value. Bio oil obtained from palm kernel seed contains 6.5% of H, 44.6% of C, 2.92% of N, and 40.20% of O along with an 18.51 (MJ/kg) heating value(Vickers, 2017). The present study is novel as *Eriobotyra japonica* seeds have not been used previously as feedstock for pyrolytic experiments in the presence of three different catalysts including red mud, Alumina, and Bentonite clay.

Experimental

Materials and Methods

Eriobotrya japonica seeds were purchased from the Local Market in Lahore, Pakistan. After washing it thoroughly, the seeds were crushed, milled, and sieved to the pore size of 0.6mm (Table 1).

Before the pyrolysis experiment, proximate and ultimate analysis of *Eriobotrya japonica* was done to evaluate the composition and potential of liquid products (Table 2). For ultimate analysis, an elemental analyzer (LECO-CHNS 932) was used. Tappi tests (Tappi T222 for lignin, Tappi T202 for hemicellulose, Tappi T211 for ash, and Tappi T264 for moisture contents) were used for the determination of the main characteristics of seeds. Higher heating value was determined by Dulong's Formula (Eq.1).

$$HHV\left(\frac{MJ}{kg}\right) = 0.3383\ x\ C + 1.422\ x\ \left(H - \frac{O}{8}\right) \qquad (1)$$

The weight % of carbon, oxygen, and hydrogen are represented by C, O, and H respectively. Table 2 shows that proximate analysis of *Eriobotrya japonica* possesses higher content of C and H and a low amount of N_2 moisture, and ash content respectively which make it appropriate for pyrolytic biomass.

Differential thermal analysis (DTA) and thermogravimetric (TG) were used for the investigation of pyrolysis parameters and Thermal performance of *Eriobotrya japonica* respectively. Approximately, 7.805 mg of raw *E japonica* material was taken for thermal analysis and heated (from 25 °C to 1000 °C at a heating rate of 10 °C per minute) with nitrogen flow at 10 mL/minute.

Experimental procedure

In this study, a stainless-steel tubular-shaped fixed bed reactor equipped with N_2 inlet was used for the pyrolysis experiments. The sample of biomass was kept in an oven at 90 °C overnight to get dried. In a typical run, about 20g of *E. japonica* seed raw material was added into the reactor and was tightly closed having just one inlet pipe for N_2 gas and one outlet pipe which was further connected to three bottles for collecting oil. Nitrogen gas at 100 mL/min flow rate was circulated during the whole pyrolysis experiment to ensure an oxygen-free environment. An external electric furnace was used for heating and a controller helped in controlling temperature whereas, the final temperature was kept constant for 30 minutes in the reactor. To provide low temperature, the bio-oil collecting bottles were kept in a salt-containing ice bath, however, the gaseous products were neither collected nor discharged.

To study the temperature parameters, the pyrolytic process, in the absence of a catalyst, was carried out at different temperatures (350, 450, and 550 °C), at a 100 °C per minute constant heating rate. The liquid was obtained and condensed in oil collecting bottles which contain two different phases: pyrolignic acid as the aqueous phase and pyrolytic oil as the oil phase, both covered by dichloromethane. This collected oil was separated from the solvent by using a separating funnel and for the calculation of bio-oil yield, it was dried in the presence of anhydrous sodium sulphate. However, the residue left in the reactor, named bio-char, was weighed and stored in sample bottles. Additionally, for the calculation of the product yield of bio-gas following calculations were used.

$$Percentage\ conversion = \frac{(Wbiomass\ - Wsolid)}{Wbiomass}\ x\ 100 \qquad (2)$$

$$Liquid\ Yield\ (\%) = \frac{Wliquid}{Wbiomass}\ x\ 100 \qquad (3)$$

$$Solid\ Yield\ (\%) = \frac{Wsolid}{Wbiomass}\ x\ 100 \qquad (4)$$

$$Gas\ yield\ (\%) = 100\% - Liquid\ Yield\ (\%)\ - \ Solid\ Yield\ (\%) \qquad (5)$$

Here, *"Wbiomass"* and "*Wsolid"* represent the weight of initial biomass and the weight of left residue (after drying), respectively.

To study the effect of catalysis, at different temperatures, three different catalysts (alumina, red mud and bentonite clay), each weighted 10 wt.%, were used by following the above method. In the end, obtained yields were calculated on an ash-free and dry basis, respectively.

To analyze the products for functional groups and characteristic peaks, GC-MS (Model: QP-2010, Shimadzu, Japan) and elemental analyzer (Perkin Elmer LECO-CHNS-932) were used at 350 °C and 550 °C.

Result and Discussion

In Fig. 1, the TGA curve shows that about 6% weight loss occurred when the temperature reached 330 °C. This weight loss represents the moisture content of the feedstock. However, Figure 1 also shows that the hemicellulose and cellulose content of *Eriobotyra japonica* material begins to decompose at 250 °C while maximum decomposition occurs at approximately 360 °C. Additionally, maximum weight loss occurred between 300-330 °C and the depolymerization of lignocellulosic material began at 250 °C - 350 °C. It is also considered as the pyrolytic zone for the lignocellulosic materials. Hence, the decomposition rate decreased gradually after 500 °C and weight loss was negligible after 800 °C which became almost zero after 1000 °C. The materials left behind after 1000 °C are ash, fixed carbon content and some other inorganic material of feedstock that were not decomposed up to this temperature. Additionally, TG weight loss and obtained derivatives curves indicate maximum weight loss. The initial decomposition temperature of raw *Eriobotyra japonica* material was gained at a much lower temperature as compared to other fruit seeds which is considered as an advantage for pyrolysis behavior. This is mainly due to the difference in the chemical composition of *Eriobotyra japonica* seeds and other biomass feedstock.

Table 1 Physiochemical properties of seed oil of *E. japonica*

Property	**Result**	**Unit**	**Test method**
Physical state	Liquid	-	-

Density @ 20ºC	0.889	g/cm^3	AOCS method Cc10a-25
Color	3.8Y	-	AOCS method Cc13e-92
Refrective index @30ºC	1.45	-	AOCS method Cc 7-25
Kinematic viscosity @ 20ºC	66.2	mm^2/s	ASTM D445
% FFA	1.66	%	AOCS method Ca 5a-40
Saponification number	193.37	mg KOH/g	AOCS method Cd 3-25
Iodine number	146.68	G I_2/ 100g oil	AOCS method Cd 1-25

Table 2 Proximate and ultimate analysis of *E. japonica* raw materials

Proximate analysis (weight % on dry basis)	
Lignin	21.43
Cellulose	36.28
Hemicellulose	32.88
Moisture	3.77
Ash	4.87
Soxhelt extractives	0.74
Ultimate analysis (weight % on dry basis)	
Carbon (C)	42.40
Hydrogen (H)	6.65
Oxygen (O)	49.45
Nitrogen (N)	1.49
Sulfur (S)	_
Higher heating value (MJ/kg)	13.98

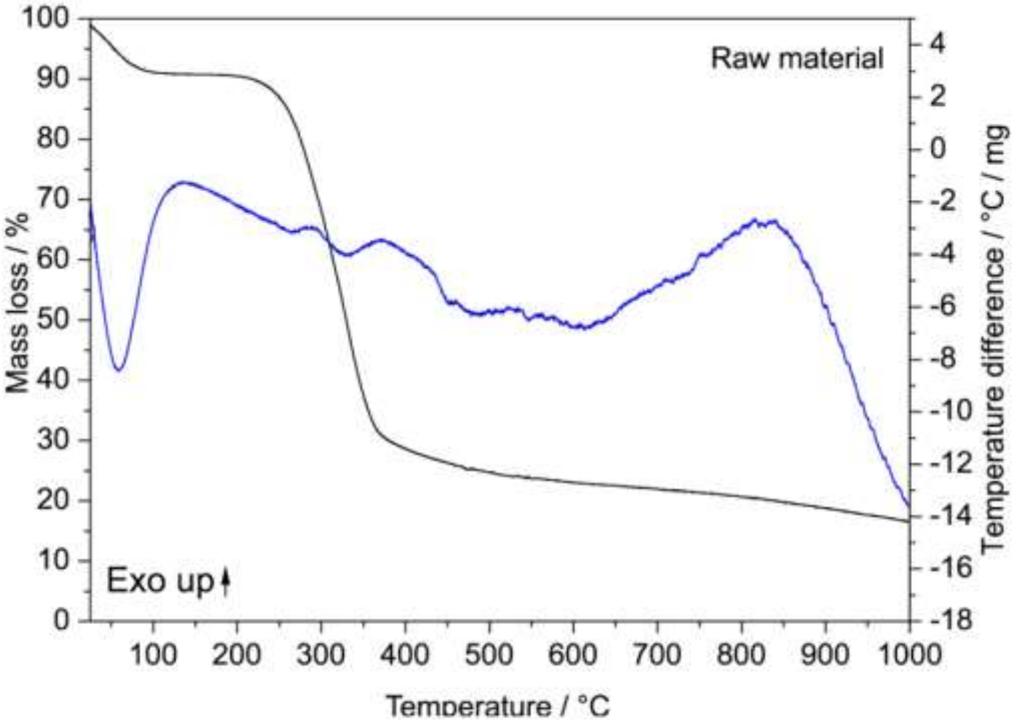


Fig. 1 TG analysis of *E. japonica* seeds biomass

Product yield and temperature

The temperature has a significant impact on the pyrolysis process of lignocellulose biomass and has a substantial influence on the amount of pyrolytic products produced. Consequently, as the temperature increases, the fragmentation of biomass also increases. The conversion of bio-oil and char products into gaseous products initiates when cracking processes occur within the temperature range of 400 -550 °C and above 600 °C. According to reports, the amounts of aliphatic, aromatic, and polar components found in bio-oil increase as the temperature rises from 300 to 500 °C and from 600 to 800 ºC (Akhtar & Amin, 2012; Kan, Strezov, & Evans, 2016).

Results obtained after pyrolysis of *E. japonica* seeds at three temperature ranges without and with (10 wt.%) catalyst are shown in Table 3. The heating rate was kept constant at 100 ^{o}C/minute with the rate of heating remaining constant at 100 °C /min and the nitrogen rate stayed aligned at 100 mL/ min. Figure 2 illustrates the experimental rounds presented in Table 3. Except for the alumina catalyst, a significant alteration in product yield is found for all of the samples. For the catalyst-free studies conducted at a temperature of 350 °C, 450 °C, and 550 °C temperatures, the liquid yield for each sample was 26.6%, 28.44%, and 25.14% respectively. The liquid yield obtained with the red mud catalyst was 28.82%, 30.35%, and 26.15%. Red mud, while serving as a useful catalyst, exhibits a decline in the production of liquid products for secondary cracking reactions after a specific temperature threshold is reached. The reactive substances transform into solid and gaseous products, resulting in an elevation in temperature. The behavior of only the alumina catalyst remained consistent as the temperature increased. The source material undergoes primary decomposition, whereas the char residue undergoes secondary decomposition, in response to variations in temperature. Furthermore, the absence of a catalyst and an increase in temperature from 350 °C to 550 °C resulted in a reduction in the product yield of biochar. A similar pattern was noted for alternative catalysts and the thermal decomposition of different types of lignocellulosic biomass.

Table 3 Products obtained by *E .japonica* seed pyrolysis at different temperatures without and with catalyst

Pyrolysis Temperature	Catalyst	%Bio oil	%Biochar	%Syngas	%Conversion
350 °C	No catalyst	26.66	33.10	40.24	66.90
	Alumina	26.18	42.20	31.62	57.80
	Red mud	28.82	37.51	33.67	62.49
	Bentonite clay	22.04	41.85	36.11	58.15
450 °C	No catalyst	28.44	29.41	42.16	70.6
	Alumina	28.83	35.94	35.23	64.06
	Red mud	30.35	36.02	33.63	63.98
	Bentonite clay	28.67	35.7	35.61	64.10
550 °C	No catalyst	25.14	25.96	48.90	74.04
	Alumina	34.69	33.24	32.07	66.76
	Red mud	26.15	35.11	38.14	64.29
	Bentonite clay	28.57	31.94	39.49	68.06

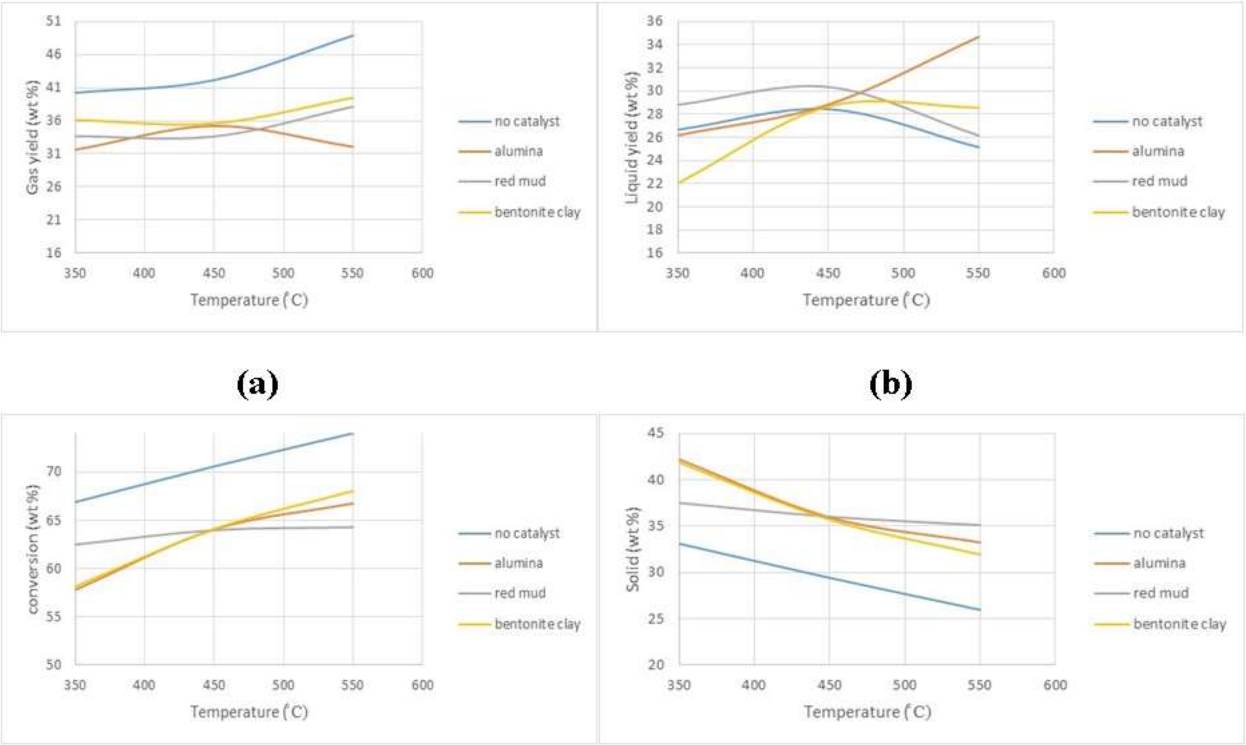
Product yield and effect of catalysts

The catalyst has a significant influence on the product yield, as well as its composition and dispersion (S. Wang, Dai, Yang, & Luo, 2017). Some recorded data suggests that catalysts have a beneficial impact on the pyrolysis of biomass. However, another study contradicts this, demonstrating a decrease in product yield like the presence of an acidic catalyst during the pyrolysis of palm kernel shell led to a decrease in the production of bio-oil and an abnormal increase in the production of gas products due to the catalytic transformations of volatile chemicals. The process of catalytic deoxygenation and aromatization of volatile substances results in decreased molar ratios of hydrogen to carbon and oxygen to carbon. Compared to fossil fuels, this bio-oil had higher concentrations of nitrogen, sulfur, and oxygen (Carvalho, Cunha, Pereira, & Ataíde, 2015).

Not all catalysts have an equivalent impact on the production of solids, liquids, and gases (Fig. 2). The synergistic impact of a catalyst becomes apparent when comparing the temperature of a catalyzed experiment to that which runs in the absence of the catalyst. The difference in yields between runs with catalysts at temperatures of 450 °C and 500 °C was minimal but significant compared to runs without catalysts. Red mud at a temperature of 450 °C resulted in a higher product yield. The red mud resulted in the highest product yield of 30.35%, while the yield without catalyst was 28.44%. The addition of bentonite clay resulted in a yield of 28.67%. The maximum liquid product yield of 34.69% was obtained with alumina at a temperature of 550 ℃. Alumina is an acidic catalyst often employed in the pyrolysis of biomass to facilitate the cleavage of C-O and C-C bonds. This occurs as a result of ring opening, depolymerization, and dehydration. The inclusion of alumina leads to the degradation of cellulose and hemicellulose polymers, resulting in an increase in gas production and a decrease in char formation. An acidic catalyst induces the removal of water from pentosyl residues, glucosyl, and anhydrosugars, resulting in an increased production of furfural. Pyrolysis is a process in which both primary and secondary reactions are facilitated by a catalyst (Di Blasi, Branca, Galgano, & Zenone, 2015; S. Wang et al., 2017).

The rate of hydrogen transfer processes is closely correlated with the acidity of the catalyst. These reactions are crucial for the production of H_2 gas. The product yield remains constant in all experimental runs, regardless of the presence or absence of a catalyst. However, as the temperature increases, the product yield falls. When bentonite clay was present, the solid product yield reached its greatest value of 41.85% at a temperature of 350 °C. In contrast, without any catalyst, the lowest yield of a solid product was observed at 25.96% at a temperature of 550 °C. Heterogeneous catalytic processes employ metal oxides as support, promoters, and active components for various objectives. The presence of flaws in crystal structures gives rise to versatile features in various metal oxides. Pyrolysis of metal oxides with acid-base surfaces results in the generation of diverse compounds (S. Wang et al., 2017).

Gas generation increases linearly with increasing temperature in all experiments, except for alumina at 550 °C. The experiment conducted without a catalyst resulted in a maximum yield of 48.90% at a temperature of 550 °C. The gas formation percentages with alumina were 31.62%, 32.07%, and 35.23%. It was hypothesized that alumina undergoes partial hydrolysis when reacting with the substrate, resulting in the production of HCl by the release of H_2O, and catalyzing the reaction process.



(a) **(b)**

(c) **(d)**

Fig. 2. Effects of catalysts and temperature on product yield of *E. japonica* seeds biomass

Characterization of pyrolysis products by NMR, elemental, and GC-MS

Hemicellulose, cellulose, and lignin have a significant impact on biomass pyrolysis. The lignin has a suppressive and repressive impact on the thermal polymerization patterns and carbonization of macromolecular products, such as levoglucosan, which is generated during cellulose pyrolysis. Lignin aids in the decomposition of cellulose into smaller molecules. Cellulose inhibits the production of char and facilitates the conversion of lignin into phenols. The interactions between lignin and hemicellulose facilitate the synthesis of phenols caused by lignin and inhibit the development of hydrocarbons. The connection between cellulose and lignin is of more significance than the interaction between cellulose and hemicellulose in herbaceous plants. As a result, the rate of levoglucosan reduces while the levels of low molecular compounds and furans increase(Zhang et al., 2015). Several researchers have reported on the interplay of three fundamental components in biomass, although the underlying process remains elusive. Approximately 50 constituents have been recognized in the process of biomass pyrolysis, including maltose, glucose, carbohydrates, and cellulose, among others. Levoglucosan is the fundamental pyrolysis product of cellulose, which is present in all saccharides. By examining the decomposition products of cellulose through pyrolysis at temperatures ranging from 350 °C to 600 °C. Below a temperature of 400 °C, anhydrosugars were identified as the primary compounds, whereas at higher temperatures, formic acid and levoglucosan were determined to be the predominant compounds (Patwardhan, Satrio, Brown, & Shanks, 2010; Z. Wang, Wang, Cao, & Wang, 2010).

The seeds of *E. japonica* were subjected to pyrolysis, both with and without a catalyst. The resulting liquid products were then analyzed using elemental analysis, NMR spectroscopy, and GC-MS. The solid products were analyzed using elemental analysis. The elemental analysis results for bio-oil and bio char obtained at three distinct temperatures, namely 350 °C, 450 °C, and 550 °C, are presented in Tables 4 and 5, respectively. The carbon content of bio-oil ranges from 44.34% to 59.32%, while the higher heating value (HHV) fluctuates between 25.99 and 16.89 MJ/Kg (Table 4). The carbon content of HHV value ranges between 23.54-15.88MJ/Kg and bio char varies between 76.41%-55.45%. Furthermore, it was noted that there was a rise in the Carbon ratio, a decline in the Oxygen ratio in char and liquid products, and higher values of HHV products were also achieved in comparison to the raw material. The oxygen concentration in bio-oil was reduced as a result of catalytic deoxygenation through the production of CO_2 and CO. The most preferable method for removing oxygen in the context of bio-oil's H/C ratio is by the utilization of CO_2. This approach proves to be highly effective in reducing the oxygen content. The components targeted for oxygen removal include cellulose, hemicellulose, furans, and anhydrosugars such as levoglucosan1,4,3,6-Dianhydro-A-D-glucopyranose,1-hydroxy-3,6-dioxabicyclo (3,2,1) Octan-2-one can be attained by the process of dehydration of sugar. Several important and advantageous chemicals can be synthesized by transforming these substances (Fabbri, Torri, & Mancini, 2007).

Alumina proved to be a highly effective catalyst for the higher heating value (HHV) of biochar. Bentonite clay proved to be the most efficient catalyst for enhancing the higher heating value (HHV) of bio-oil. Alkaline earth metals exhibit greater Lewis acidity and are found in bentonite clay, which enhances the hydration processes involved in the synthesis of sugar molecules. Bio oil is a complex mixture of organic compounds. These compounds belong to 4 different groups including aliphatic, monoaromatics, oxygenated compounds, nitrogenated compounds, and derivatives. Nitrogenated compounds contain amides and amines like pyrimidine, pyridine, and thiazole. The majority of phenolic chemicals and their derivatives are produced by the degradation of lignin and can be identified using gas chromatography-mass spectrometry (GC-MS)(Adam et al., 2006). The compounds in question comprise methoxy phenols, phenols, cresols, alkyl phenols, and guaiacol. Bio oil, obtained via pyrolysis, has diverse applications, including its use as biofuel. Bio oils consist of a variety of ketones, esters, ethers, and aldehydes. Phenols are highly valued for their significant economic importance. Cellulose degradation also yields these chemicals. The bio-oil contains a significant amount of ethanol derivatives, acetic acid, furan derivatives, and decane derivatives. In this investigation, a total of 44 and 53 distinct compounds were identified in the bio-oil samples obtained at temperatures of 350 °C and 550 °C, respectively. The observed differences could be attributed to secondary reactions, such as cracking and re-polymerization, that occur as the temperature increases.

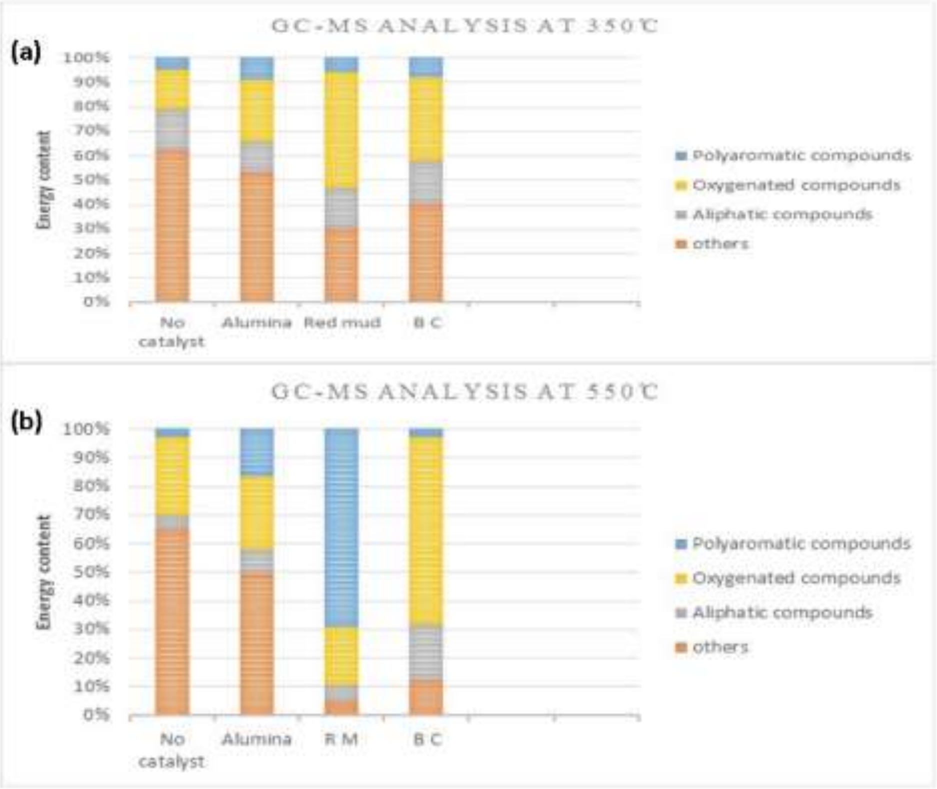


Fig. 3 GC-MS analysis of bio oils (a) at 350 ^{O}C (b) at 550 ^{O}C

Fig. 3 graphically represents the presentation of liquid products, including aromatics, oxygenated chemicals, and aliphatic. The catalyst and temperature have a discernible impact on the resulting product from pyrolysis. The highest yield was seen at a temperature of 550 °C, but at 350 °C, the presence of red mud catalyst resulted in the highest concentration of oxygen compounds, reaching 47.22%. Alumina produced the greatest amount of polyaromatic compounds, while bentonite clay yielded the highest percentage of aliphatic compounds at 14.05%. At a temperature of 450 °C, the concentration of monoaromatic compounds reached its peak at 72.17% when using bentonite clay as the catalyst. The use of bentonite clay resulted in the highest levels of oxygenated and aliphatic compounds, while the lowest levels of polyaromatic compounds were observed. The results obtained at a temperature of 550 °C were comparable to those obtained at other temperatures. The use of Red mud catalyst resulted in the highest proportion of monoaromatic compounds, with a percentage of 69.09%. Bentonite clay yielded the highest amounts of oxygenated and aliphatic chemicals, with percentages of 65.75% and 20.01% respectively. The maximum production of polyaromatic compounds achieved a yield of 15.33% using alumina as a catalyst. The results have verified that alumina is suitable for the creation of polyaromatic compounds, whereas bentonite clay is effective in the presence of oxygen and aliphatic compounds.

The results of the H-NMR analysis are presented in Fig. 4. The spectra display the presence of protons belonging to the aromatic group, which are observed between the peaks at 8.5 and 6 ppm. The chemical shifts of the protons in the methoxy and carbohydrate groups are recorded within the range of 6.0 to 4.4 ppm. The protons of alcohol and methylene dibenzene groups are identified by the peaks observed at chemical shifts between 4.4 and 3.0 ppm. The aliphatic peak is observed in the chemical shift range of 3.0 to 1.5 ppm. The maximum concentration of alkane groups is detected within the range of 1.5 to 0.5 ppm.

Changes in the highest values were detected in basic chemicals during GC-MS analysis. The detected mesomeric effect was more dominant than the prior one. The chemical shift values were affected due to the presence of a combination of hydrocarbons and oxygen in the bio-oil. Structural degradation and cleavage of compounds might arise according to the reaction circumstances (Çolak, Durak, & Genel, 2018).

Table 4 Elemental analysis of bio-oil at 350 °C, 450 °C and 550 °C

Pyrolysis Temperature	**Compounds**	**Without Catalyst**	**Alumina**	**Red mud**	**Bentonite clay**
350 ^{o}C	Carbon (C)	56.71	46.47	49.21	59.32
	Hydrogen (H)	8.11	6.99	7.84	7.21
	Nitrogen (N)	0.65	0.28	0.69	0.89
	Oxygen (O)	36.59	47.23	44.51	34.65
	H/C molar ratio	1.75	1.96	1.59	1.51
	O/C molar ratio	0.53	0.77	0.68	0.41
	High heating value (MJ/Kg)	25.53	18.55	18.21	25.99
450 ^{o}C	Carbon (C)	47.32	49.42	52.92	57.54
	Hydrogen(H)	7.61	8.42	7.34	7.20
	Nitrogen (N)	0.67	0.49	1.87	1.65
	Oxygen (O)	43.93	42.79	39.66	31.38
	H/C molar ratio	1.78	1.81	1.54	1.49
	O/C molar ratio	0.71	0.67	0.60	0.33
	High heating value (MJ/Kg)	17.99	18.99	18.43	23.69
550 ^{o}C	Carbon (C)	56.21	44.34	50.89	47.97
	Hydrogen (H)	7.98	8.57	6.84	6.21
	Nitrogen (N)	0.51	0.78	0.41	0.73
	Oxygen (O)	38.49	44.31	46.57	45.31
	H/C molar ratio	1.67	1.92	1.96	1.72
	O/C molar ratio	0.61	0.73	0.79	0.75
	High heating value (MJ/Kg)	23.41	18.33	16.89	17.41

Table 5 Elemental analysis of bio-char at 350 °C, 450 °C and 550 °C

Pyrolysis Temperature	**Compounds**	**Without Catalyst**	**Alumina**	**Red mud**	**Bentonite clay**
350 ^{o}C	Carbon (C)	69.92	57.52	51.54	55.45
	Hydrogen (H)	2.59	2.65	2.59	3.47
	Nitrogen (N)	0.48	0.58	0.52	0.89
	Oxygen (O)	25.94	39.84	36.01	40.89
	H/C molar ratio	0.41	0.57	0.46	0.70
	O/C molar ratio	0.32	0.52	0.47	0.57
	High heating value (MJ/Kg)	21.44	16.13	17.02	15.99
450 ^{o}C	Carbon (C)	76.41	64.07	57.04	69.28
	Hydrogen (H)	2.62	2.56	2.02	2.06
	Nitrogen (N)	0.56	0.69	0.51	0.89
	Oxygen (O)	21.82	34.62	39.30	26.03
	H/C molar ratio	0.42	0.49	0.46	0.38
	O/C molar ratio	0.30	0.43	0.51	0.31
	High heating value (MJ/Kg)	17.49	23.54	16.39	20.67
550 ^{o}C	Carbon (C)	73.64	61.95	63.54	64.83
	Hydrogen (H)	1.76	1.28	1.62	1.79
	Nitrogen (N)	0.38	0.44	0.54	0.67
	Oxygen (O)	24.35	37.77	38.53	33.28
	H/C molar ratio	0.38	0.32	0.38	0.30
	O/C molar ratio	0.31	0.47	0.38	0.41
	High heating value (MJ/Kg)	22.29	15.88	16.10	15.79

Table 6 Analysis of pyrolysis oil obtained at 350 °C **with and without catalyst by GC-MS**

Compounds	**no catalyst**	**Alumina**	**Red mud**	**Bentonite clay**
Guaiacol	0.61	0.85	0.54	0.72
Benzeldehyde, 2,4-dimethyl-	1.66	0.35	-	-
Furfuryl alcohol	0.32	0.40	0.32	0.44
Cyclododecasiloxane, tetracosamethyl-	3.35	-	-	-

Propanoic acid	1.23	0.35	0.91	0.43
Phenol-4-ethyl-2-methoxy	0.18	0.21	0.18	0.21
Furan, 2,5-dimethyl-furan	0.44	-	-	-
Acetic acid	0.81	1.34	-	0.75
Phenol	0.45	0.56	-	0.63
Trichloroacetic acid, 3-tridecyl ester	0.83	-	-	-
Cyclododecasiloxane, eicosamethyl-	0.43	-	-	-
(2E)-2-Butenedioic acid	0.47	-	-	-
1,4,7,10,13,16—hexaoxacyclononadecane	32.27	44.46	24.99	5.86
2,6-Dimethoxyphenol	2.09	-	1.45	-
2-Methoxy-4-vinylphenol	0.22	-	-	-
Benzoic acid	0.74	-	-	-
18,18-Bi-1,4,7,10,13,16-hexaoxacyclononadecane	11.6	6.76	7.37	42.25
Gamma-butyrolactone	-	1.27	-	-
2-Furancarboxaldehyde, 5-methyl	-	0.37	-	-
2-Furancarboxaldehyde	-	0.38	-	0.29
N-Nitrosodimethylamine	-	0.22	-	-
Octaethylene glycol monododecyl ether	-	18.44	-	-
Timolol	-	0.49	0.46	0.42
1,2-Cyclopentnedione	-	0.22	-	-
Ethylcyclopentenolone	-	0.34	-	-
Dodecyl acrylate	-	-	0.15	-
3,3-Dimethyl-2,4-pentane dione	-	0.19	-	-
2-Cyclopentene-1-one, 2-hydroxy	-	-	0.26	-
2(3H)-Furanone, dihydro-	-	-	0.16	0.19
Urea	-	0.32	-	-
2-Pentanone, 4-hydroxy-4-methyl-	-	-	0.30	0.59
1,4,7,10,13,16,19-Heptaoxacyclohenicosane	-	4.62	-	3.29
Dodecyl acrylate	-	-	0.47	-
3,3-Dimethyl-2,4-pentane dione	-	-	0.17	-
Phenol, 2.4-bis(1,1-dimethylethyl)	-	-	0.12	-
Diethylthioacetal of aldehyde desoxy-isoteviol	-	-	-	10.58
Phenol, 2-methoxy-4-methyl	-	-	-	0.61
3-Methyl-1-hexene-3-ol	-	-	-	0.41
2(5H)-Furanone,5-methyl-	-	-	-	0.36
Heptaethylene glycol monododecyl ether	-	-	-	0.11
Pyridine, 3-methoxy	-	-	-	0.42
Octaethylene glycol	-	-	6.69	-
Furoxan, 4-nitro-3-phenyl, 2-oxide	-	-	16.88	-

Table 7 Analysis of pyrolysis oil obtained at 550 °C with and without catalyst by GC-MS

Compounds	**no catalyst**	**Alumina**	**Red mud**	**Bentonite clay**
2-Pentanone, 4-hydroxy-4-methyl-	0.30	0.64	0.46	-
Cyclopentanone,2-methyl	0.33	-	-	-
Furfuryl alcohol	0.18	0.10	-	0.67
Guaiacol	0.76	0.12	1.98	0.89
2,4 Dimethylbenzaldyhyde	0.78	-	-	-
Thiazole dimer	0.31	-	-	-

Cyclooctane, 1,2-dimethyl	0.59	-	-	0.78
Acetic acid	0.81	1.34	-	0.75
Phenol	0.25	0.48	-	0.98
Phenol, 4-ethyl-2-methoxy	0.61	0.34	0.45	0.28
Benzocyclooctene, 7,8-dimethyl	1.27	-	-	-
Phenol, 2,4-bis(1,1-dimethylethyl)	0.31	-	-	-
2,6-Dimethoxyphenol	1.95	-	-	-
Phenol, 2-ethyl-	0.23	-	-	-
(5E)-5-Methyl-5-hepten-3-one	0.69	-	-	-
Furfural	-	0.22	0.33	-
2(5H)-Furanone,5-methyl	-	0.15	-	-
Furoxan, 4-nitro-3-phenyl, 2-oxide	23.94	3.83	-	-
Propanoic acid	0.1	0.28	0.35	0.45
2-Furancarboxaldehyde	-	0.38	-	0.29
2(5H)-Furanone	-	0.78	0.45	0.32
Gamma-butyrolactone	-	0.45	1.56	-
1-Methyl-2,3-cyclohexadione	-	0.33	0.98	0.03
2,3,5-Trimethylfuran	-	0.40	0.20	-
2-Cyclopenten-1-one,3-ethyl-2-hydroxy	-	0.26	-	0.18
2-Propylpiperidine	-	0.21	-	-
1,2-Cyclopentanedione, 3-methyl-	-	0.85	1.31	0.60
2-Cyclopentene-1-one, 3-ethyl-2-hydroxy	-	0.92	0.67	-
2-propylpiperidine	-	0.12	0.17	-
phenol, 2-methoxy-4-methyl	-	0.29	0.67	-
Tetradecyl acrylate	-	0.43	-	-
Decyl acetate	-	0.41	-	-
m-cresol	-	0.77	0.47	-
Phenol, 3,5-dimethyl	-	0.55	-	-
phenol, 3,4-dimethyl	-	0.20	0.84	0.43
2-Methoxy-4-vinylphenol	-	0.63	-	-
Phenol, 2-methoxy-4-methyl	-	-	-	0.61
2,6-Dimethoxyphenol	1.54	3.73	-	2.70
Phenol, 2,4-bis(1,1-dimethylethyl)	-	0.08	0.12	-
4-Pyranone, 2,3-dihydro	-	-	0.52	0.19
3,6-Dimethoxy-2-ethylbenzaldehyde	-	10.77	-	-
Octaethylene glycol monododecyl ether	-	6.80	-	-
Octaethylene ether	-	7.99	-	-
1-Methylcycloheptaanol	-	-	0.32	-
4-Bromo-2-methylbenzoic acid	-	0.50	-	-
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	-	-	16.37	-
Methyl 2-methyl-1-deuterio-2-propenyl ether	-	0.16	-	-
2-Pentanone, 1-hydroxy	-	-	-	0.17
2-Furancarboxaldehyde	-	-	-	0.16
Ethylene oxide heptamer	-	-	-	8.80
Butanoic acid	-	-	-	0.39
Pyridine, 3-methoxy	-	-	-	0.18

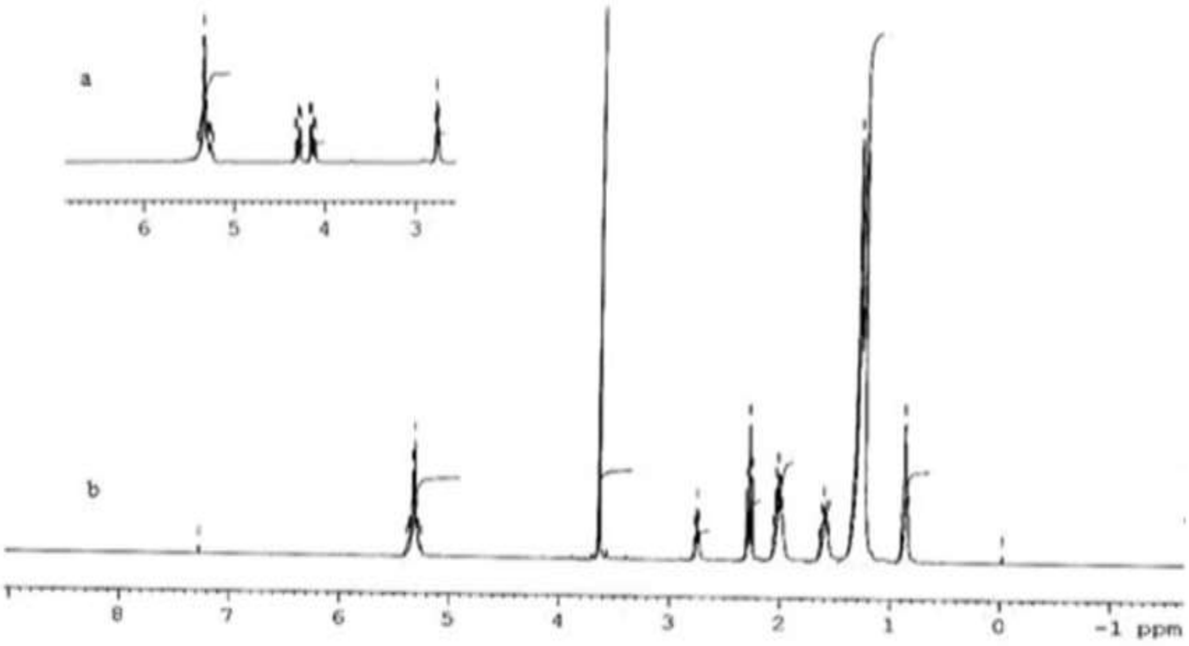


Fig. 4 (a) H-NMR of *E. japonica* seed oil (b) H-NMR of biodiesel of *E. japonica* seed oil

Fuel properties of E. japonica biodiesel

The fuel characteristics of biodiesel derived from E. japonica seed oil were analyzed using ASTM D6751 standard techniques. The obtained values fell within the specified range. The kinematic viscosity value was elevated at 5.5 mm 2/sec, which significantly impacts fuel spray, combustion, and mixture formation.

The fuel characteristics of biodiesel derived from E. japonica seed oil were analyzed using ASTM D6751 standard techniques. The obtained values fell within the specified range. The kinematic viscosity value was elevated at 5.5 mm 2/sec, which significantly impacts fuel spray, combustion, and mixture formation. The use of low volatility fuel in conjunction with high viscosity can lead to issues such as ignition delay, misfire, and difficulty starting the engine in cold weather. The cold weather characteristics of gasoline can be assessed by examining its pour point and cloud point. An acid number exceeding 3% might result in pump deposition, which in turn leads to corrosion. The cetane number is a crucial measure of fuel quality, and a value exceeding 65 results in rapid ignition of gasoline near the injector, leading to excessive heating. The intense heating causes the production of cooked particles in the injector, resulting in the obstruction of the injector nozzle. A prolonged ignition delay results in the occurrence of diesel knock. The Cu-strip corrosion and distillation temperature were observed to fall within defined thresholds. The seed oil of *E. japonica* has the potential to be used as a feedstock for the production of biodiesel. The values have been condensed and presented in Table 8.

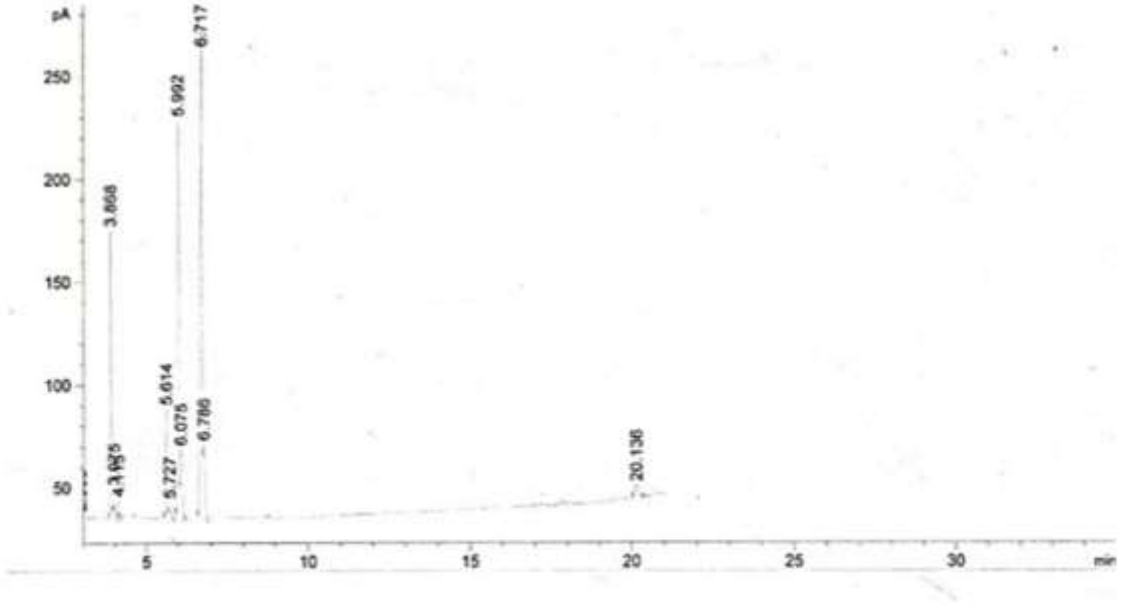


Fig. 5 Chromatogram of *E. japonic*a seed oil

Table 8: Fuel properties of *E. japonica* biodiesel

Property	ASTM test method	Result	Unit	ASTM limit
Flash point	D 93	137	°C	93 min
Acid value	D 664	0.36	mg/ KOH/g	0.50 max
Cloud point	D 2500	-3	°C	Report
Pour point	D 97	-6	°C	--
Cetane number	D 613	50	-	47 min
Cu strip corrosion	D 130	1	-	No. 3 max
Kinematic viscosity@40 °C	D 445	5.5	mm^2/sec	1.9-6.0
Distillation (90% vol. recovery)	D 1160	346	°C	360 max

Conclusion

The current study examined the impact of temperature and catalysts on the conversion of *E. japonica* seed oil into liquid and solid products through the process of pyrolysis. The investigation was conducted without a catalyst and with three different catalysts: Alumina, Red mud, and Bentonite clay. The temperatures tested were 350 °C, 450 °C, and 550 °C. The liquid and solid products were analyzed by GC-MS, elemental analysis, and H-NMR. The analysis of the data confirmed that the higher heating value (HHV) of the liquid products fell within the range of 16.89-25.99 MJ, while the HHV of the solid products ranged from 15.88-22.29 MJ. According to the energy values, it was found that a temperature of 550 °C was more efficient for the catalyst compared to other temperatures. The results obtained from GC-MS and H-NMR were mutually corroborative. Therefore, it was deduced that the seed oil extracted from *Eriobotrya japonica* can be transformed into high-energy products through pyrolysis, making it a viable alternative energy source.

CRediT Author Statement

Conceptualization, Investigation, methodology and analysis were done by **Alizzah Amanat and Iftikhar Hussain** whereas drafting, editing, reviewing and analysis were done by **Farrukh Bashir, Muhammad Tasaeen, Muhammad Shahid, Zile Huma, Nelofer Jamil and Muhammad Aamir Raza.**

Conflict of interest

The authors affirm the absence of any conflicting interests.

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