242. Production of Biofuel by Hydrothermal Liquefaction of Date Palm Seeds

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Abstract

Pakistan is a rich country in the date palm production and hence a large amount of date seeds is generated still now there is no any proper solution to utilize these seeds, it was observed that these seeds have great potential for the conversion to biofuels owing to its abundance and favourable composition .Hydrothermal is the wet pyrolysis process of biomass, a new idea of co-solvent hydrothermal liquefaction was performed using the methanol with water that could successfully produce the yield of Phenolic compounds. Purposed based equipment was designed and fabricated in which process parameters can be observed easily. Bio-char is by-product of this process which has higher amount of fixed carbon and calorific value than that of parent date palm seeds; bio-char has great importance as solid bio fuel. The parameters observed were reaction time (10-30 min) and residue time is 24 hours, reaction temperature (110ºC to 220ºC), methanol water ration (1:1 to 2:1), NaOH concentration in water (0.95M- 1.8M) NaOH acts as catalyst.

Keywords: *Hydrothermal Reactor, Bio-char, Product yield, Palm date seeds*

1. Introduction

The increasing demand for energy has tend to exhaustion of fossil fuel sources [1],that may cause to deplete soon due to continuous use since long [2]. And an increase in energy demand also leads an increase in crude oil prices which will effect on the world economy [3].these reasons led to a move towards renewable sources of energy that should be sustainable, efficient and cost-effective energy [4]. It has been observed that among the renewable sources that can be sustainable for fossil fuels biomass is second to none. Abundance, environmental friendly, sustainable and low cost has promoted biomass to gain more attention for research [5]. In the past, biofuel used to be produced from edible resources like soybeans, canola oil, animal fat, palm oil, corn oil and low grade cooking oil and jatropha oil [6]. However, attempts are now made towards biofuel production from non-food crops, microalgae macro algae [7] .Bio oil from date palm seeds is a promising new source biofuel. Dates have been a staple diet in the Middle East and Pakistan for thousands of years [8]. The world production of dates has increased considerably during the last 30 years. Indeed, the production has tripled from 2,289,511 tons in 1974 to 6,772,068 tons in 2004 [9]. Pakistan one of the top ten countries in palm date cultivation ,total cultivation area for palm dates is about 223880 acres and production is about more than 531200 tones (in 2010); mostly three districts are major date producers kahairpur, gawadar and turbat districts[10].

Preliminary process studies on the conversion of various types into liquid fuels have indicated that hydrothermal upgradation (HTU) is more attractive than pyrolysis or gasification. [17]. Hydrothermal reaction produces three types of products gaseous products , liquid bio-oil and solid bio char ,the gaseous products are not observed here in this work , when liquid bio-oil is main product the process is called as hydrothermal liquefaction and when the [11]. The chemistry of hydrothermal liquefaction is complicated and highly substrate dependant and will be addressed in the following sections. The main products are bio crude with a relatively high heating value, char, water-soluble substances and gas. Addition of various alkaline catalysts can suppress char formation and thus improve oil yield and quality. As the temperature is increased above that of the critical point of water, gasification becomes the dominating

process [12]. In this study the hydrothermal process was applied in the presence of alkali (NaOH) solution and methanol to get phenolic and ketonic compounds in the liquid yield.

2. Materials And Methods

2.1. Date seeds biomass collection

Area of khairpur district was selected for the material collection; raw material (dates) was purchased from local market of kairpur city. The seeds were physically isolate from fruit by hands. Seeds were soaked in tape water for 2 hours and then washed several times with distilled water to remove any remaining date material. Later then seeds were air dried at room temperature and then dried in oven at 105ºC for 24 hours to remove the moisture present in seeds. The dried seeds were ground and sieved and particle size for reaction was selected 4500µm<x<5000 µm

2.2. Reactor fabrication and configuration

A purposed based autoclave reactor was fabricated to carry out the reaction. The high pressure stainless steel (SS 316) autoclave reactor with a capacity of 3.5L [1]. This autoclave reactor is 40cm deep and diameter of 24cm, maximum temperature and pressure capacity are 500ºC and 100 bars respectively. At the top of the reactor condensing vessel was fixed with mechanical press machine ice is placed in the condenser to condense the high pressure vapours in the autoclave reactor, tow valves have to be fixed for inlet and out let of chill water in case of chiller connection, the temperature range of chilled water is from 3 ºC to 8 ºC. A 2500 Watt heater was used for heating purpose, tow bimetallic thermocouples are to be installed in the equipment one is for the temperature reading of reactor the range of this thermometer is up to 400 ºC and second thermometer is for the condenser that can sense up to 100 ºC. The pressure gauge at the top of reactor vessel is installed that can measure the pressure of up to 10 bars. Two valves at the top of the reactor are fitted one is for gaseous products collection and other is for nitrogen purging and both valves are optional. A turbine Stirrer with 5cm wide and 1.75cm thick connected with a 25cm long shaft with 400rpm rotation was used to mix the reactants uniformly during the reaction.

2.3. Testing methods and Raw material characterization of palm date seeds

The physical and chemical characteristics of the raw palm date seeds and Hydro char was examined to observe the effect of raw material on hydrothermal reaction. Moisture content was determined according to the ASTM E1358 -97 (2013) in microwave oven at 105 ºC. Ash content was measured by ASTM method numbered E1755-01(2015) by combusting the biomass at 650 ºC for 6 h in open crucibles on a dry weight basis. The volatile matters was determined by placing dry biomass inside a muffle furnace at 550ºC for 12 h to measure mass loss due to volatilization of volatile components. While fixed carbon content was calculated as the residue remaining after volatile matter release in the biomass. The elemental analysis was performed to measure the carbon, hydrogen, nitrogen and oxygen by using the stable Isotope elemental analyser, all calculations and measurement was observed in triplicates at room temperature (23 $\pm$ 2), Gas Chromatography and Mass spectroscopy (GC-MS) test was performed to get the analysis of bio-oil liquid

The Palm date seeds have low ash content as 1.14% moisture is about 8.9% and it was observed that these seeds have higher volatile materials that are about more than 65% and about 25% fixed carbon this composition of seeds shows that palm date seeds have great ability to produce a good quality of bio-oil liquid fuel the solid bio char as by product produced form hydrothermal reaction have higher calorific value than that of parent seeds. The results of raw date seeds and solid biochar are given in *table 1.*

Table 1. Ultimate and proximate analysis of raw palm date seeds and biochar at different temperature

Parameter	Raw date seeds	Bio char at 170 ºC	Bio char at 200 ºC	Bio char at 220 ºC
Moisture content %	8.9	9.1	6.7	5.2
Ash content %	1.14	1.2	1.1	0.9
Volatile content %	65.4	43	42	40.2
Fixed carbon content %	24.8	34	36.2	39.1
C %	28.3	31	33.3	34.8
N %	0.7	1	0.8	0.6
H %	7.35	6.4	6.1	6.8
Higher Heating value (Mj / Kg)	11.3	15.8	19.2	21.2

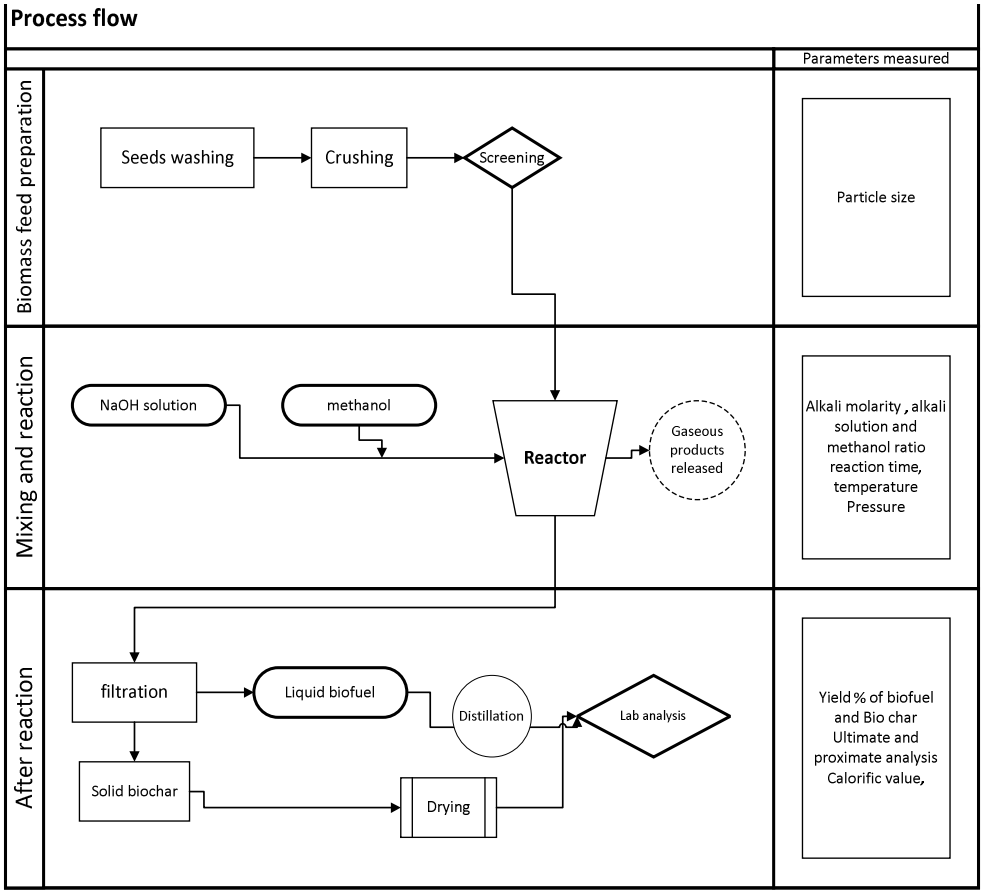


Fig. 1. The process flow diagram of bio-oil and solid residue production from palm date seeds

2.4. Biofuel preparation

Alkali solution of NaOH was prepared with concentration of 1.5 Molarity in demineralized water mixed with methanol in various ratios ranges from 1:1 to 3:1by vol% and bio mass to cosolvent ratio ranges from 1:3 to 1:6 crushed seeds with particle size between 4500µm to 5000µm and this solution was poured into the reactor for reaction. Cosolvent with 1:1 ratio and prepared biomass feed sample was mixed the ratio of cosolvent to biomass was 1:3 in high pressure autoclave reactor the mixture was stirred with agitator at 350 rpm to mix the solution and biomass feed before starting the reaction .

The reactor was heated with connected heater with increase rate of temperature at a 10ºC per minute. The chilling water was circulated at the top condenser to control the pressure in this way solvent vapour that was continuously produced by heating the mixture was condensed and returned to bottom of reactor and again vaporized. The chilling water circulation was started, the inlet chilling water temperature was 5ºC to 8ºC and circulation chilling water rate was 10 to 12 litres per hour the reaction temperature was ranging 130 ºC to 210 ºC and reaction time was 20 minutes to 40 minutes in the series of experiments. Then the heater was switched off and reactor was cool at room temperature when the reactor achieves the 25$\pm$1 ºC the product in the form of slurry of solid residue and bio-oil were removed from reactor manually, the gaseous products were not observed and therefor they were vented out. The solid filter cake that is biochar was placed in oven at 250ºC for 12 hours to dry it then both products liquid bio- oil and solid bio char was further characterised. The flow diagram of the process is given in fig 1.

2.5. Yield percentage

Products of the reaction, liquid bio-oil and solid biochar that were weighed and yield percent of the product from palm date seeds were calculated by the following equations

$$\text{Yield of bio-oil (wt. \%)} = (W_{bl}/W_f) \times 100 \quad (1)$$

$$\text{Yield of biochar (wt. \%)} = (W_{ch}/W_f) \times 100 \quad (2)$$

3. RESULTS AND DISCUSSION

In this reaction of date palm seeds with alkali NaOH solution and methanol, two different products was achieved we have liquid bio-oil and solid biochar we have considered the bio-oil as main product and solid biochar as by product and both have the different effects of measuring parameters (like temperature, cosolvent ratio, NaOH concentration and time) on yield percent from the reaction.

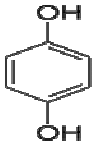
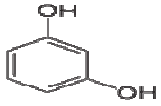
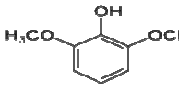
Table 2. Effects of alkali solution to methanol, time, temperature, concentration of NaOH on Yield percent of bio oil liquid

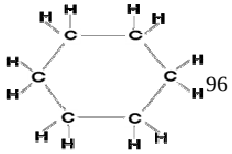
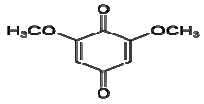
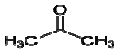
Run	Alkali solution to methanol ratio	Time (min)	Temperature (°C)	Concentration of NaOH in M (mole /litre)	yield %
1		20	150	0	9
2	01:00	30	150	0.95	27
3		20	220	0.95	35
4		10	110	0.95	20
5		30	150	0.95	31
6		30	180	1.5	68
7		30	210	1.5	81
8	01:01	10	160	1.5	48
9		30	200	1.5	76
10		20	180	0.4	21
11		20	170	1.8	77
12		30	220	1,6	80
13	02:01	20	180	1.5	42
14		30	200	1.5	58
15	01:02	30	180	1.4	69
16		20	180	0.95	61

3.1. Liquid bi-oil

The liquid bio-oil product produced from the hydrothermal liquefaction of palm date seeds contains a verity of organic compounds as shown in *Table 2.* Mostly phenolic and ketonic compounds are generated, these compounds that generated by HT reaction in the presence are higher than that of compounds generated from the HT reaction only in water [xiv] it is due to the solubility of lignocellulosic material of palm date seeds in the methanol solvent

Table 3. Gas Chromatography and Mass Spectroscopy (GC-MS) analysis of liquid bio-oil from hydrothermal reaction of palm date seeds

Peak No	Retention Time (min)	Relative Composition by percentage area (%)	Compound name	Structure	MS-quality (%)
1	1.752	43.82	Phenol		95
2	2.314	12.65	1,4-benzenediol (Hydroquinone)		94
3	3.687	8.47	1,3 benzenediol		93
4	4.358	8.56	2,6-dimethyoxyphenol		97

5	5.42	6.26	cyclohexane		96
6	6.389	8.34	*n*-propanol	$CH_3CH_2CH{=}O$	94
7	7.489	6.77	2,6 dimethoxybenzoquinone		93
8	8.899	5.13	di methyle ketone		95

3.2. Effect of temperature

In the hydrothermal reaction temperature is the main parameter which effects on yield percentage of liquid bio-oil and solid residue [xiv]. The different ranges of temperature(110ºC to 220 ºC) was studied to observe the decomposition of lignocellulose material ,lignin and cellulose material are to be decomposed from lignocellulosic material in Hydrothermal reaction up to 200 ºC as water soluble fraction [xiii] . The palm date seeds are lignocellulosic material with the composition as: 50% lignin and 20% cellulose [xv]. It has been observed that the higher the reaction temperature higher the liquid bio-oil yield however, the liquid yield percentage may reduce after specific temperature range at where the liquid product is decomposed and gaseous products are generated [xvii]. As shown in *Table 3*.the minimum yield% is at 110ºC and higher amount of yield is at 220 ºC (below the critical point of methanol). While the solid residue (biochar) yield decrease with increase in temperature this can be seen from the fig 3.it is due to the decomposition of solid material at higher temperature.

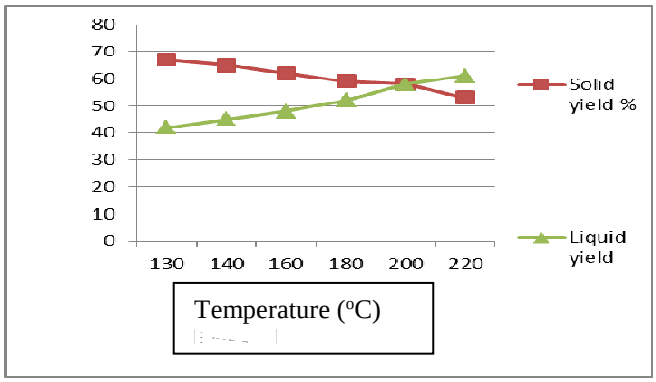


Fig. 3. Effect of temperature on yield % of liquid bio-oil and solid biochar and at 1:1 ratio of water to methanol

3.3. Effect of alkali solution and solvent ratio.

The ratio of alkali solution to the solvent (methanol) has major effect on the yield of liquid bio-oil yield, because both have great ability to decompose the biomass which helps for new product formation. Alkali solution acts as the catalyst in the hydrothermal reaction [xvii] because NaOH is the good digester for the organic materials; while the methanol solvent dissolves the organic materials like protein 5.56%, oil 10% and total carbohydrates 83% [xvii] in the seeds are mostly soluble in the methanol and hence it helps to increase the rate of reaction by addition of heat to it. It can be seen form the fig 4.that yield percent is minimum in the only in distilled water and it increase with increase in NaOH concentration and solvent ratio

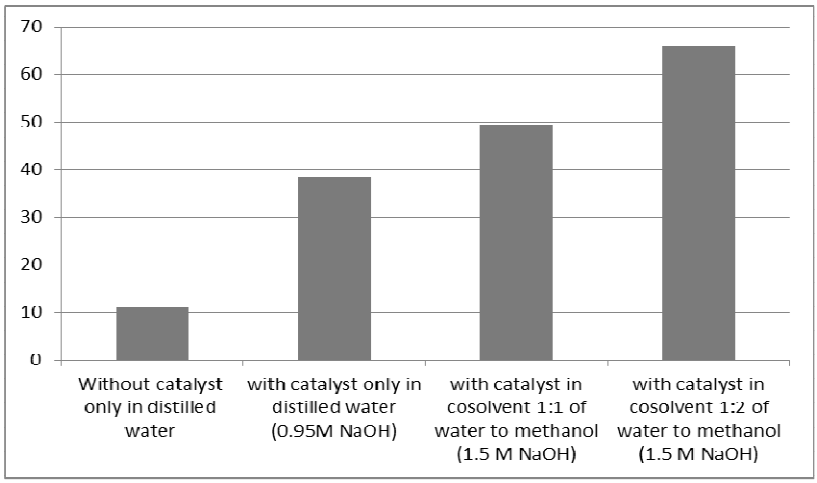


Fig. 4. The effect of solvent methanol and alkali solution on the yield percent

3.4. Effect of reaction time

Reaction time is also an important factor which effects on the yield of liquid bio-oil and solid bio char [xvi], experimental results given in table *2.* Shows that the yield percent increase with increase in reaction time while solid biochar yield decrease with increase in reaction time as shown in fig 5 (a) and fig 5(b)

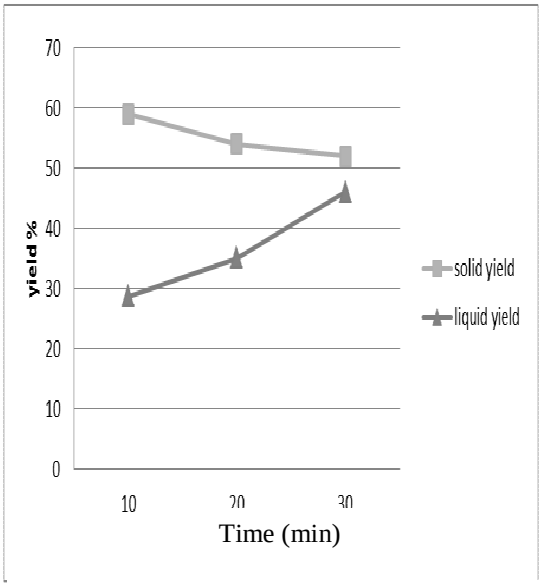


Fig. 5 (a). The effect time on liquid bio-oil and solid biochar yield (reaction only in distilled water)

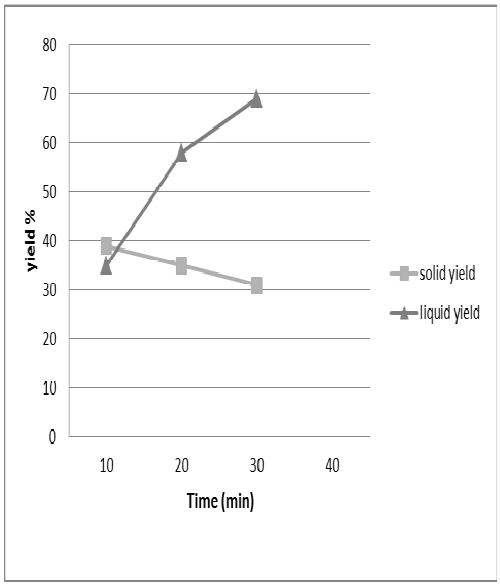


Fig 5 (b). The effect time on liquid bio-oil and solid biochar yield (reaction in 1:2 alkali solution to methanol ratio in 1.5M concentration of NaOH)

4. Conclusion

Palm date seeds have a great efficiency to produce the bio-oil liquid fuel and solid biochar by hydrothermal reaction in the presence of methanol solvent and NaOH in different proportions. The production of liquid bio-oil and biochar depends up on the temperature, concentration of alkali base methanol solvent to water ratio. As the concentration of alkali solution, ratio methanol to water and time increases the yield percent will also increase. The liquid bio-oil yield contains a different phenolic ketonic and cyclic alkane compounds.

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