

Hydrothermal Liquefaction of Sorghum Bagasse for Maximization of Bio-Crude using Homogeneous Catalyst (Na_2CO_3)

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Research Article

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Abstract

This work investigates the feasibility of hydrothermal liquefaction process for synthesis of biocrude to produce bio-oil from sorghum bagasse, in the presence of a homogenous catalyst and solvent. An extensive evaluation of potentially available sorghum bagasse is carried in the presence of a homogenous catalyst (sodium carbonate) and solvent to produce bio-oil. The optimal operating conditions in the ranges of temperature (220°C-280°C), reaction time (15-60min), biomass to water (1:10), biomass to catalyst (1:10%), biomass to glycerol (1:10) are chosen, for evaluating the process. The optimal conditions of temperature (260°C) and residence time (60 minutes), biomass: water: glycerol ratio (1:5:5) have achieved a maximum yield of 52.16%. The bio crude oil when evaluated using various physio chemical chemical processes like elemental analysis indicated the presence of higher carbon, lower sulphur and nitrogen contents. The chemical composition of bio-oil when determined using *CHNS*, *FTIR* and *GC-MS* analysis and when qualitatively characterized and indicated the presence of phenols, ketones, carboxylic acids and esters.

Novelty Of This Research Article

The main objective of this paper is to maximize the bio-oil yield with homogeneous catalyst (Na_2CO_3). Even though many researchers were worked on the homogeneous catalysts such as K_2CO_3 , KOH , NaOH etc. using HTL process, but no one were worked on Na_2CO_3 as catalyst and also the optimum bio-oil yield of 52.16 wt% at 260°C with 60min retention time. Finally, we concluded that compared to other researchers work in this study at low temperature only we have got highest bio-oil yield.

1. Introduction

The consistent demand for energy with simultaneous concern for environment and climatic changes along with unsustainable fossil fuel resources has attracted the human mankind to produce renewable and clean energy. Renewable energy derived from solar, hydro, tidal, wind, and geothermal fuel sources which is alternative conventional fossil fuels have enormous potential to sustain an eco-friendly approach is required to consolidate bio-economy. Among these energies, bio-fuel produced from biomass with high carbon content at low cost has an imperative role among renewable energies. The demand for bio-fuels globally has necessitated the development of technologies based on energy crops without affecting food security and environment. Biomass derived from agricultural residues, energy crops, aquatic plants etc., are an ideal carbon resource for the production of first generation bio-fuels like bio-ethanol and bio-diesel (A.R.K Gollakota et al., 2018), chemicals and advanced bio-fuels (bio-hydrogen, bio-gas, bio-oil, bio-char, syngas etc.) Biomass is derived from organic material such as trees, plants, agricultural residues and urban waste comprising stalks, straws, leaves, seeds, nut shells, roots etc. It is subjected to various conversions, bio/ thermochemical conversions techniques to produce energy and biofuels. The agri waste includes straws of rice, wheat, sorghum, bajra etc, with sorghum being an important cereal crop grown globally that can be grown in multiple environments having drought tolerance. It is in the form of a grain with sweet, forage and low-lignin content present in abundance at

the researchers place, near telanganga, india. (Olivera S. et al., 2020) Sorghum (*Sorghum bicolor* L) is an important staple cereal crop with high photosynthetic efficiency, which is mostly grown under rain fed conditions in marginal lands and can be effectively used as a feedstock for the production of biofuels or chemicals (Yang Yue et al., 2018). Numerous researchers (Zheting, Bi et al., Varsha Niroula., Thabo, z et al.,) have worked on conversion of sorghum biomass into various products. (Olivera S. et al., 2020), have presented overview on conversion methodologies of sorghum biomass into liquid fuels (ethanol, diesel and oil), gaseous fuels (hydrogen, bio-gas and syngas) and solid fuels (bio-char). They have narrated in detail, the developments of various pretreatment conversion process and fermentation processes. They have also analysed the complete lifecycle analyses which indicate the challenges, opportunities that augment the proficiency, benefits and tasks in various steps in problems and solutions. The biomass is converted into bio-oils using thermochemical process like combustion, gasification, pyrolysis and direct liquefaction, where the biomass is pressurized to high pressures. HTL (Christensen et al., 2014) is an emerging technology in conversion of biomass to bio-oils and is particularly useful for wet feedstocks like organic residues, sludges, and is a direct liquefaction process involving high pressures (5–24 MPa), moderate temperatures (250–375°C), presence of water just below its critical point, absence of oxygen with or without catalyst to produce bio-crude as the major product and small amount of byproducts like solid, gas and aqueous phases were resulted in the presence of water. The yields of bio-oils derived from HTL depends on the source of biomass, operating conditions, initial solvents, catalysts etc. The applicability of wet biomass in HTL directly without thermal heating is an advantageous outcome compared to other processes and in reduced cost analysis. (Yang et al., 2014) and without chemicals (Leichang Cao et al., 2016; Christensen et al., 2014; Gan and Yuan, 2014) and less corrosivity (Cybulska et al., 2010). A brief and short review on HTL is narrated by (Gollakota A.R.K et al., 2018). An HTL process on lignocellulosic biomass at 200–350°C, 5–30 MPa was done by and have achieved excellent results on bio-oil yield in comparison with (Cybulska et al., 2010). Lignin a by product of biomass was subjected to HTL to obtain oligomers by (Yuan et al., 2007) using phenol and sodium hydroxide as solvent and at a temperature 260°C for residence time of 60 min. (Liu et al., 2008) used pinewood with various solvents obtained the optimum bio-oil yield of 26.5 wt% with a 20 minutes retention time. (Shuna, C et al., 2010) derived bio-oil from pine saw dust using HTL with various co-solvents such as water, ethanol and methanol, comparison of these 3 the most efficient solvent is water. (Shuana et al., 2020) used white pine sawdust to achieve the maximum yield of 65 wt% at 300°C for 15 min using two different solvents like water and alcohol. A similar study on saw dust was explored by (Flabianus H et al., 2017) at temperature (180–260°C), reaction time (0–2h) and to yield an aqueous product yield of 57.2 wt%. The effect of co-solvent on rice straw with varied biomass to solvent ratios and catalysts were explored by (Yerrayya et al., 2020) to obtain a bio-oil yield of 12.3 wt% at 300°C with 18 MPa pressure in 60 min and also identified that the yield increased by 36.8 wt% using methanol. (Demirbas et al., 2008) have obtained similar observations using sawdust with different solvents like Na₂CO₃ and NaOH in the range of temperature 440 to 560K. Similarly, above mentioned researcher used hazelnut shell as biomass with the temperature (250–330°C) and solvent, finally resulting the bio-oil yield decrease with high temperatures. (Yang et al., 2014) conducted HTL on solid biomass at 200–350°C temperature, 5–30 MPa pressure to generate bio-crude without oxygen be used as a transportation fuel, which compared is less corrosive than that

reported by (Cybulska et al., 2010). Similarly, the works of (Yuan et al., 2007) using water, sodium hydroxide and phenol for degradation of high molecular weight lignin into oligomers at 260°C for 60 min have resulted in successful results. The concept of micro reactor technology for HTL was carried by (Zhe Zhu et al., 2018) barley straw with potassium carbonate into the production of bio-crude. The process variables such as temperature, time, catalyst and biomass to water ratios were further optimized with central composite design (CCD) to achieve the optimum condition at 304.8°C, 15.5 min with the bio-oil yield of 38.72 wt%. The effect of cosolvents HTL of rice straw process was studied by (Leichang Cao et al., 2016) in a high-pressure batch reactor. The results on analysis were found that 5 wt% of Na₂CO₃ at 260°C for 1 h, achieved a bio-oil yield of 50.31 wt%. The effect of CuZnAl catalyst on the yield of monomeric phenols like 2,6-dimethoxy-phenols and 4-ethyl-phenol based on bio crude derived from rice straw was studied by (Zhou, C et al., 2016) at yield 26.8wt% at temperature 300°C and reaction time 30 min. (Syamsul Hadi et al., 2014) obtained bio-fuel from rice husk using ethanol as solvent in a HTL process at 325°C and reaction time of 30 minutes. The resulting biooil with an optimum yield 36.3 wt% was further analysed for physical properties, which indicated in the presence of lighter fuel oils with a calorific value (12.1–20.2 MJ/kg), viscosity (1.11–1.6 cSt), and flash point (14–29°C). The bio-oil yield of 65 wt % was obtained at 300°C with alcohol for 15min. Conversion of biomass to bio-oil above 300°C temperature repolymerization occurs. The present researchers, (Monika Kashimalla et al., 2021) in their current research have explored using biomass as sorghum bagasse with the effect of process parameters such as temperature (220 to 280°C), time (15 to 60 min) with Na₂CO₃ catalyst were systematically studied and analysed CHNS, FTIR and GC-MS. To optimize the process CCD was used with the process parameters. The maximum yield of 45.23 wt% was obtained at 260°C for 60 min.

In this work, the researchers initiated this process as there is very little research found in the application of HTL for sorghum bagasse. (Zheting Bi et al., 2017) produced bio-oil from sweet sorghum bagasse using HTL process with various catalysts like potassium carbonate (K₂CO₃), potassium hydroxide (KOH), formic acid (CH₃COOH), Ni/SiAl, Ni₂P and zeolites at 300 and 350°C. They observed that the three catalysts K₂CO₃, KOH, and Ni/SiAl have resulted in higher yields of bio oil (61.8%, 42.3% and 45.0%) with low yields of biochar at 300°C, with K₂CO₃ leading to higher heating value (HHV) of 33.1 MJ/kg. Similarly, (Varsha Niroula 2014) have used sweet sorghum bagasse with and without catalyst to produce biooil using HTL under varying temperatures, catalyst concentrations and reaction times. The process without catalyst has resulted in a bio oil of 7.517%, which has been significantly improved to 45.28% with K₂CO₃ catalyst. The experimental results were fitted to a cubic model, which on prediction has achieved the yield of 57% with potassium carbonate (K₂CO₃) at 320°C for 60 min. The resulting bio-oil was analysed by CHNS analysis with high carbon and low sulphur content. Table 1 indicates the studies conducted by various researchers on application of HTL process to sorghum biomass.

In the present work, HTL for production of bio-oil with sorghum biomass is conducted and the results are analysed to achieve the desired yields.

Table 1
Literature survey on sorghum

S.No	Feedstock	Operating conditions	Solvent/co-solvent	Catalyst	Bio-oil yield %	References
1	Sorghum bagasse	300–350°C	water	K ₂ CO ₃ , KOH, formic acid, Ni/Si-Al, Ni ₂ P and zeolite	45% @ K ₂ CO ₃ @ 300°C@60min	Zheting Bi, Ji Zhang etc
2	Sweet sorghum bagasse	300°C	water	K ₂ CO ₃	45.28%@ K ₂ CO ₃ @300°C @60 min	VarshaNiroula
3	Sweet sorghum bagasse	260–320°C	NaOH	53.2 wt%@320 °C	Thabo,z. Sehume, christien. Strydom etc.

1.1. Process mechanism of HTL

HTL (Leichang Cao et al., 2016) process consists of conversion of biomass into bio-oil which is a multi mixture of carbohydrates, lignin, proteins, and lipids is depolymerized into crude oil involving several stages like depolymerisation, decomposition and recombination at molecular level through decomposition, depolymerisation and is particularly advantageous for wet biomass which is highly heterogeneous and complex. In HTL process, the biomass is decayed and de-polymerized into smaller molecules that are highly reactive, to form bio-oil, solid residue and gaseous products. The various process inputs governing process like pressure, temperature, residence time, repolymerization, condensation etc needs to be monitored and controlled. Biomass undergoes depolymerisation where in the biomass is sequentially dissolved, with the underlying hemicellulose and cellulose biopolymers undergo a thermal stability change contributing to the formation of bio oil. At high pressure and temperature, the long C-H-O bonds will be reduced to shorter chains, with energy changes in presence of water. Subsequent to depolymerization, decomposition takes place comprising dehydration, decarboxylation and deamination. Reduction of water, carbon dioxide and amino acid is likely to occur in dehydration, decarboxylation and deamination. The macromolecules present in biomass are hydrolyzed to oligomers and monomers. Glucose monomers are generated from cellulose due to the presence of water at high temperature and pressure. It is understood that the presence of fructose in contrast to glucose, degrades rapidly into valuable products due to various reactions like isomerisation, hydrolysis, dehydration, reverse-aldol defragmentation, rearrangement and recombination reactions etc. The products like polar organic chemicals, furfurals, glycoaldehydes, phenols and organic acids are observed to have highly solubility in water.

2. Materials And Methods

2.1 Materials

Sorghum bagasse, the chosen biomass in this study was procured from telangana region and it is pulverized to a particle size of 3–4 mm. Sodium carbonate (Na_2CO_3) as catalyst, glycerol as co-solvent and ethyl acetate as solvent (EA) for separation were purchased from sigma Aldrich in lab grade.

2.2 Feedstock Characterization

Sorghum bagasse was characterized by elemental (ultimate, proximate and structural) composition. The ultimate analysis was conducted with elemental analyzer based on ASTM D-5373 to determine the elements carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) composition appear in Table 2, in which by the difference of oxygen was calculated. The proximate analysis was obtained by using ASTM E-870-06 to find out various contents like volatile matter (VM), fixed carbon (FC), ash and moisture content (MC) were resulted on a dry basis.

Table 2
Elemental composition of sorghum bagasse

Ultimate analysis		Proximate analysis		Structural analysis	
C	44.77	Fixed carbon	16.12	Cellulose	36.89
H	6.301	Volatile matter	72.03	Hemi cellulose	18.06
N	0.05	Moisture content	6.89	Lignin	15.66
O	48.86	Ash content	3.65		
S	0.013				
HHV (MJ/Kg)	15.58				
HHV: Higher heating value.					

The higher heating value (HHV) of sorghum bagasse was found with an Eq. (1). The structural analysis was determined by using National Renewable Energy Laboratory (NREL) comprised in the percentage of cellulose, hemi cellulose and lignin respectively.

$$HHV = 0.3383C + 1.442 \left(H - \frac{O}{8} \right) + 9.428S(1)$$

2.3 Methods

Figure 1 shows the schematic diagram of HTL process, which is 250 ml stainless steel autoclave reactor and it consists of mechanical stirrer, gas inlet and outlet valve, K-type thermocouple, a manometer and Fig. 2 defines the detailed material balance and process flow diagram of HTL.

2.4 Proposed Methodology

Experimentation was carried out in a stainless steel autoclave reactor with high pressure as shown in Fig. 1 consists of capacity 250 ml high pressure reactor (SS 316), which is provided with a jacket for circulating the cool water with the support of heating coil for heating the reactants. Briefly to, 3g of sorghum bagasse followed by 15ml water and 15ml glycerol was added with 10wt% of sodium carbonate was loaded into the reactor. The sorghum bagasse to solvent ratio was 1:10 (w/w). The reactor was firstly sealed and 2 times flushed with nitrogen to the desired pressure maintained to 1 MPa. Subsequently, heating was continued to attain the required temperature of 220 to 260°C for a reaction time of 15-60min with magnetic stirring at 300rpm. The corresponding pressure is obtained in the range of (20–60 bar). The contents of the reactants were cooled to attain room temperature by circulation of cold water, venting of gas and subsequent washing with ethyl acetate (EA). The product mixture liquid and solid phase was recovered by vacuum filtration via filter paper.

The liquid phase is extracted using a separating funnel to separate the aqueous and EA solvent phase, followed by rotary evaporator to remove excess EA and water under pressure at 80 and 90°C. The resulting residue which is mostly solid was dried in an oven at 105°C for 12hrs to be weighted and analysed for determination of the composition and analysis.

2.5 Yields of products

Conversion of bio-oil, solid residue, gas and liquid product fractions were determined as follows.

$$\text{Bio - oilyield}(wt\%) = \frac{\text{weightofbio - oil}}{\text{weightofinitialbiomass}} * 100(2)$$

$$\text{Solidresidueyield}(wt\%) = \frac{\text{weightofsolidresidue}}{\text{weightofinitialbiomass}} * 100$$

3

$$\text{Gasandaqueousproductsyields}(wt\%) = 100\% - \text{bio - oilyield} - \text{residueyield}(4)$$

2.6 Bio-crude characterization/Analysis

2.6.1 Fourier Transform Infrared Spectroscopy (FT-IR)

FTIR spectra of bio crude was analysed by using spectrometer (SHIMADZU IR Prestige 21) used to recognize the functional groups of liquid, solid and gas. The spectra have been registered in the range of 400-4000 cm^{-1} with resolution of 2 cm^{-1} , potassium bromide disc. A total of 40 scans were made to get a better signal to noise ratio. To identify the chemical compounds scan the samples by using infrared light.

2.6.2 Gas chromatography-Mass Spectroscopy (GC-MS)

Gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) is a column chromatography analysis to identify the chemicals by using chem station software was carried out with a model of 5973 N using an Agilent 6890 with mass selective detector. Capillary column (HP-5MS) with 30m length and 250 μ m internal diameter was used. Initially the column temperature was increased from 50 $^{\circ}$ C to 280 $^{\circ}$ C with hold up time at 10 $^{\circ}$ C min⁻¹ ramping and maintained flowrate 1.2ml/min with the support of helium gas with split ratio of 10:1. All the identified compounds were analyzed based on GC-MS conditions.

3. Results And Discussion

3.1 Experimental procedure

Sorghum bagasse with experimental conditions used 3gm biomass, 15ml water as solvent, 15ml glycerol act as co-solvent, 10wt% of sodium carbonate acts as catalyst and the ratio of biomass to water is 1:10. Table 3 defines the different temperatures (220, 240, 260, 280 $^{\circ}$ C) and residence times (15, 30, 45, 60 min) with the conversion of products such as bio-crude, solid residue.

Table 3
Influence of temperatures w.r. to times using constant catalyst dosage

Run	Temp (°C)	Time (min)	Catalyst dosage (wt %)	B:W	Pressure (bar)	Bio-oil yield (wt %)	Bio-char yield (wt %)	Gas + Aqueous yield (wt %)
1	220	15	0.3	1:10	24.5	6.65	52.63	40.72
2	240	30	0.3	1:10	35.1	10.06	42.45	47.49
3	260	45	0.3	1:10	50	17.31	38.79	43.9
4	280	60	0.3	1:10	57.9	13.52	44.52	41.96
5	220	15	0.3	1:10	24	7.88	46.31	45.81
6	240	30	0.3	1:10	35.3	10.67	39.22	50.11
7	260	45	0.3	1:10	49.9	19.17	35.16	45.67
8	280	60	0.3	1:10	58.8	14.67	40.89	44.44
9	220	15	0.3	1:10	23.5	8.67	42.21	49.12
10	240	30	0.3	1:10	35.3	11.24	38.65	50.11
11	260	45	0.3	1:10	50	20.45	31.74	47.81
12	280	60	0.3	1:10	58.9	15.12	37.63	47.25
13	220	15	0.3	1:10	24.8	9.33	34.66	56.01
14	240	30	0.3	1:10	35.7	12.62	29.24	58.14
15	260	45	0.3	1:10	49.9	21.52	21.28	57.2
16	280	60	0.3	1:10	59	17.83	31.92	50.25

Note: B- Biomass, W- Water.

Figure 4 shows bio-oil and solid residue yields with varying temperatures and retention times. It was observed that where in Fig. 4, shows the bio-oil yield increased with increasing temperature 220°C to 260 while the solid residue decreased (Ankit, j et al., 2021) and later on the temperature increased from 260 to 280°C the bio-oil yield decreased slightly due to repolymerization and hydrolysis takes place in HTL reaction (Gai et al., 2015; Tran, 2016). As shown in Fig. 4 above the maximum bio-oil yield and solid residue yield were 21.52 and 52.63 wt%.

3.2 Effect of Time

Reaction time is an imperative parameter for the production of bio-oil yield from sorghum bagasse. As a result of, the effect of reaction time (Yan, Xiu et al., 2018) on the product yields from the HTL of sorghum bagasse as biomass and retention times of (15, 30, 45 and 60 min). The bio-oil with 6.65–21.52

wt% yield increased with increasing retention time (15 to 60 min) and temperature (220 to 280°C) as mentioned detailed in Fig. 5. At 260°C the maximum bio-oil yield 21.52 wt% was observed with 60 min retention time, while the solid residue (reference) yield which decreased from (52.63 to 31.92 wt%).

3.3 Effect of reaction temperature

Many researchers worked on influence of temperature from biomass to bio-oil yield (Yan, Xiu et al., Yi Heng Chan et al., Jana, K et al., Ankit, J et al.). As shown in Table 4 it describes the effect of temperature on product yields at constant retention times and the figure shows the bio-crude yield increases as temperature is increased, the opposite was observed for solid residue yield decreased.

Table 4
Varying on temperatures with constant time and catalyst

Run	Temp (°C)	Time (min)	Catalyst dosage (wt %)	B:W:G	Press (bar)	Bio-oil yield (wt %)	Solid residue yield (wt %)	Gas + Aqueous yield (wt %)
1	220	60	0	01:10:00	26.10	4.23	58.63	37.14
2	240	60	0	01:10:00	35.50	17.68	49.45	32.87
3	260	60	0	01:10:00	49.70	28.02	42.33	29.65
4	280	60	0	01:10:00	55.00	21.83	50.12	28.05
5	220	60	0.3	01:10:00	21.20	20.68	51.89	27.43
6	240	60	0.3	01:10:00	27.20	26.83	46.21	26.96
7	260	60	0.3	01:10:00	35.70	37.02	38.28	24.70
8	280	60	0.3	01:10:00	48.50	22.33	43.33	34.34
9	220	60	0.3	01:00:10	24.20	24.48	49.56	25.96
10	240	60	0.3	01:00:10	39.20	28.96	40.24	30.80
11	260	60	0.3	01:00:10	50.50	43.58	34.92	21.50
12	280	60	0.3	01:00:10	58.20	36.54	41.74	21.72
13	220	60	0.3	01:05:05	22.80	30.14	42.89	26.97
14	240	60	0.3	01:05:05	35.40	35.33	32.68	31.99
15	260	60	0.3	01:05:05	50.20	52.16	28.92	18.92
16	280	60	0.3	01:05:05	60.00	40.12	36.54	23.34

Note: B- Biomass, W- Water, G- Glycerol

As compare to these 16 runs (catalytic and non-catalytic) the optimum conditions were obtained. Figure 6 (d) shows that attaining bio-oil yield to maximum extent of 52.16 wt% at 260°C with 60min decreases the solid residue. Zhe Zhu et al., 2014 reported that there is a possible impact on temperature, additional increase in temperature from 260 to 280°C bio-oil yield decreased due to cracking and repolymerization.

3.4 Effect of solvent

In hydrothermal liquefaction water act as a reactant or solvent, and also reaction medium for biomass conversion. Based on these conditions water has attractive properties such as high solubility and low viscosity of organic substances. An optimum was attained at 260°C, 60min time with equal ratios of water and glycerol (50%:50%) and it is shown in Fig. 6(d). These are higher than the reported work of Yi Heng Chana et al., who have carried a similar work on the effect of water as solvent with glycerol-water solutions of 50%, water as 100% and 100% glycerol.

3.5 Effect of the Biomass loading

Water acts as a reactant for the decomposition of lignocellulosic biomass to improve the bio-oil quality, as the conversion of biomass with optimum loading is examined a prominent boundary. Numerous researchers (Yan, Xiu et al., Yi Heng Chan et al., GamzeNur, A et al.,) investigated on the effect of biomass to water ratio on the hydrothermal liquefaction process, even though the process depends on parameters like temperature, time, catalyst and co-solvent in the synthesis of bio-oil. When the water to biomass ratio once reaches the limit, the bio-oil yield decreases due to high amount of water, which is possibly because of repolymerization. Hence, to find out the suitable biomass to water ratio is very important to decrease the cost. In this study, worked on sorghum biomass/water ratio is increased from 1:1 to 1:10 wt/wt, further increased the water content, the bio-oil yield decreased and solid residue continuously decreased when increasing biomass to water ratio (1:1 to 1:15). However, the optimum condition is obtained at sorghum bagasse to water ratio of 1:10 wt/wt for the production of highest bio-oil yield. The HHV of bio-crude increased with increase in sorghum bagasse to water ratio (1:1 to 1:10), and then decreased with increasing Sorghum to water ratio (1:15). The results showed that a high biomass/water feedstock ratio was usually not suitable for the liquefaction of sorghum bagasse (Yerrayya, A et al., 2020). As shown in Table 4, the biomass to water ratio is (1:10) and then the bio-oil yield increased while the solid residue yield decreased. Figure 6 shows the effect of sorghum bagasse to water ratio the maximum yield was obtained at 260°C, 60min.

3.6 Effect of co-solvent (Glycerol)

In HTL process glycerol is an attractive co-solvent and it is more efficient than the solvent for the production of bio-oil, and it is an important source to produce bio-fuels. Glycerol is completely miscible with water, the dielectric constant of water and glycerol is (46.5&78.4). Moreover, glycerol alone is not a suitable co-solvent for the production (Leichang Cao et al.,) of bio-oil using hydrothermal liquefaction process. Hence, the optimum condition was obtained at 50:50 the compositions of glycerol: water.

3.7 Effect of Homogeneous catalyst

The important role of a catalyst is dependent on the several parameters like temperature, reaction time, solvent etc. The utilization of catalyst can decrease reaction temperature, pressure increase the amount of oil and decrease the solid residue yield. Yang Yue et al., 2018, studied HTL to examine the production of bio-oil yield and quality. The main streams of catalysts are classified as homogeneous and heterogeneous. Homogeneous catalysts easily dissolved in water and it comprise in the form of alkali salts, like Na_2CO_3 , K_2CO_3 , KOH or NaOH to improve the bio-oil yield from biomass. In this study, 5wt% of Na_2CO_3 was used as catalyst for HTL of sorghum bagasse at different temperatures and retention times, sorghum to water ratio and water to glycerol ratio. Figure 6(d) shows the optimum bio-oil yield of 52.16 wt% with Na_2CO_3 at desired temperature of 260°C with 60min retention time and resulting highest HHV.

3.8 Bio-crude characterization

3.8.1 Elemental Analysis

Table 5 defines the ultimate analysis of the bio-crude using with (10 wt %) and without catalyst by using 5:5 ratio of water to glycerol with varying temperatures. The resulting bio-oil consists of higher carbon and lower oxygen composition than that of raw biomass to improve the higher heating value.

Table 5
Ultimate analysis of the bio-crude varying temperatures with constant time

S. No	Sample Name	Elemental composition					HHV(MJ/Kg)
		C	H	N	S	O	
1	BO-220°C @60min	46.17	5.89	0.03	0.011	47.89	15.63
2	BO-240°C @60min	47	4.92	0.031	0.010	47.93	14.42
3	BO-260°C @60min	48	5.75	0.035	0.011	46.20	16.30
4	BO-280°C @60min	47.8	5.69	0.026	0.012	46.47	16.11
5	BO-220°C @60min	47.22	6.12	0.04	0.011	46.61	16.49
6	BO-240°C @60min	48.15	4.86	0.032	0.010	46.95	14.93
7	BO-260°C @60min	48.99	5.32	0.036	0.012	45.64	16.13
8	BO-280°C @60min	50.6	5.28	0.029	0.011	44.08	16.89
9	BO-220°C @60min	48.8	6.56	0.05	0.012	44.58	18.04
10	BO-240°C @60min	49.12	4.98	0.039	0.011	45.85	15.63
11	BO-260°C @60min	49.23	5.68	0.04	0.011	45.04	16.83
12	BO-280°C @60min	50.9	5.49	0.030	0.012	43.57	17.39
13	BO-220°C @60min	49.0	6.98	0.058	0.012	43.95	18.08
14	BO-240°C @60min	49.56	5.02	0.045	0.011	45.36	15.93
15	BO-260°C @60min	50.67	5.99	0.052	0.011	43.28	18.83
16	BO-280°C @60min	51.90	5.33	0.051	0.012	42.70	17.66

BO- Bio oil, HHV – Higher heating value.

3.8.2 FTIR - (Fourier transform infrared spectroscopy)

FTIR is an enormous technique is based upon the identification of functional groups on reference spectrum matching the spectrum of unknown compounds. In this study, the optimum condition was obtained at 260°C with 60min by using Na_2CO_3 catalyst and the compounds were identified for bio-crude through ftir spectra with wave number as $4000 - 400 \text{ cm}^{-1}$. As shown in Fig. 7 the wide peak of OH group reveals the strong absorption between $3200 - 3600 \text{ cm}^{-1}$ and it is attributed to large amount of phenolic compounds. Peaks observed between $2800 - 2960 \text{ cm}^{-1}$ represents C-H stretching vibrations could be articulated, while the peak around 1400 cm^{-1} are likely assigned C = C stretching of aromatic groups. The wave numbers at $1050 - 1300 \text{ cm}^{-1}$ are considered as ether group C-O stretching.

As shown in Table 6 the resulted bio-crude at optimum condition consists of functional groups and positions. The position of the bands at (3383, 2936, 1400, 1000 and 600 cm^{-1}) based on the functional groups were represented as alcohol, aliphatic, aromatic, ether and alkene.

Table 6
FTIR functional groups of bio-crude at optimum conditions

Position of the bands	Functional groups	Possible compounds
3420	-OH (stretch strong)	Alcohols
2887, 2939	-CH, -CH ₂ , -CH ₃ (stretch strong)	Alkanes
1588, 1643	N-H bending	Amides
1413	C = C stretch weak	Aromatics
1300	C-O stretch strong	Ethers
923, 854	=C-H strong bending	Alkenes
567	C-Br stretch strong	Alkyl halide

3.8.3 GC-MS analysis

In this study, Fig. 8 shows the optimum conditions were obtained at temperature (260°C) and time (60min) and the chemical compounds were analysed using GC-MS. The Fig. 8 defines that major compounds with respect to concentration in the presence of percentage peak to identify the prominent compounds are shown in the chromatogram. Table 7 defines the major chemical compounds of bio-oil at optimum condition is qualitatively characterized resulting in the presence of phenols, ketones, carboxylic acids and esters. The most generous components containing major chemical compounds such as phenol, Phenol 2-methoxy, Phenol 3,5 dimethyl and Phenol 2,6 dimethoxy similarly for minor chemical compounds esters and alkynes were observed. In presence of catalyst the chemical compound of phenol composition is high and ketone composition is low.

Table 7
Chemical composition at optimum conditions w.r.to time and area % identified through GC-MS

S.No	RT (min)	Area %	Chemical compounds
1	3.529	09.28	1,2-Ethanediol, diacetate
2	4.113	07.56	1,2, propanol
3	7.075	09.45	Hexadecanoic acid, methyl ester
4	8.470	10.59	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-
5	8.367	12.21	2(3H)-Furanone, dihydro-5-methyl-
6	10.189	16.74	phenol
7	13.513	07.77	Phenol 2-methoxy
8	15.782	11.36	cresol
9	15.986	13.89	Phenol 3,5 dimethyl
10	20.766	10.85	2,3 dimrthyltoluene
11	25.851	11.02	Phenol 2,6 dimethoxy
Note: RT- Retention Time			

4. Conclusions

This work investigates the feasibility for HTL process in generation of biocrude from sorghum bagasse, in the presence of homogenous catalyst (sodium carbonate) and solvent is used to produce bio-oil. Extensive research can be done to segregate the value added products from bio fuel and other bio products from sorghum. The process parameters like temperature (220,240,260 and 280°C), reaction time (15, 30, 45 and 60min), 5 wt% of catalyst, biomass:water:glycerol ratio (1:10, 0:10 & 5:5) were studied and analysed. Experimental evaluation of the process has achieved a maximum yield of 52.16% at the optimum operating conditions of temperature (260°C) and residence time (60), biomass: water: glycerol ratio (1:5:5). This bio-crude had a high content of carbon and a very low content of sulphur and nitrogen these conditions based on elemental analysis. The resulting bio-oil further analysed with CHNS, FTIR and GC-MS. serve in order to identify the major components were phenols, acids, aromatic hydrocarbon and ketones. The resulting biocrude had a high content of carbon, low content of nitrogen and sulfur, but high content of oxygen. Elemental analysis of bio-crude indicated the presence of higher carbon content and lower sulphur and nitrogen content. The chemical composition of bio-oil examined using GC-MS analysis is qualitatively characterized at optimum conditions with major compounds indicating the presence of phenols, ketones, carboxylic acids and esters.

Declarations

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Competing Interests:

The authors declare no competing financial interest.

Author Contributions:

Monika Kashimalla: Catalysts preparation, synthesis and catalyst characterization, Polumati Anand: Planning, execution and PhD supervisor.

Data Availability:

The data that support the findings of this study are available on request from the corresponding author.

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Figures

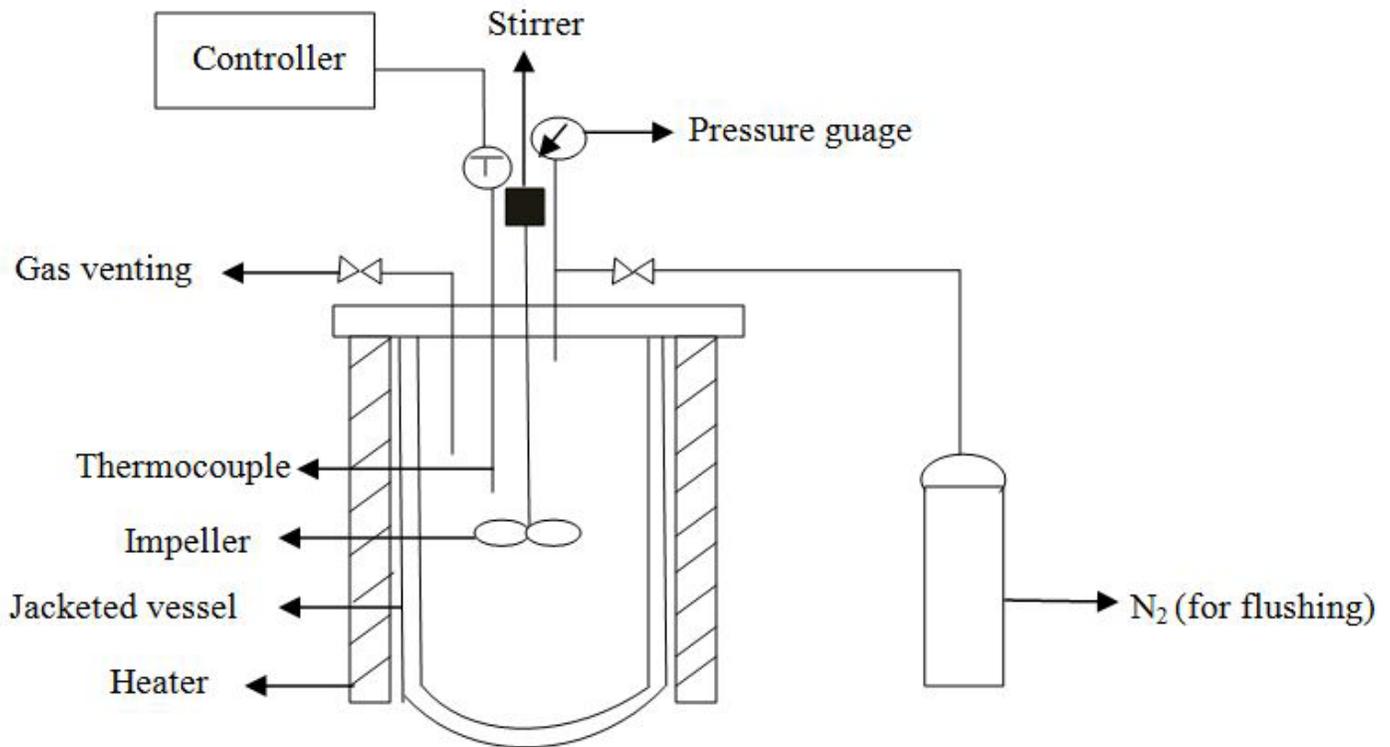


Figure 1

Schematic diagram of hydrothermal liquefaction (HTL)

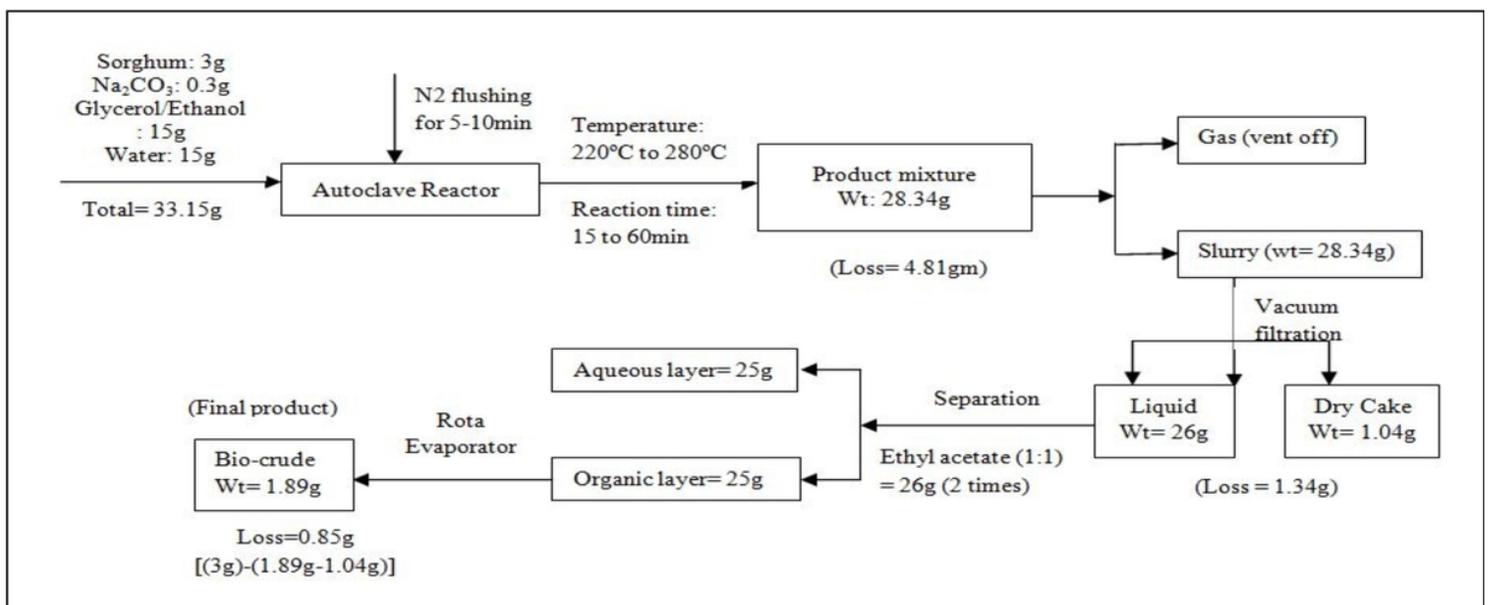


Figure 2

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Figure 3

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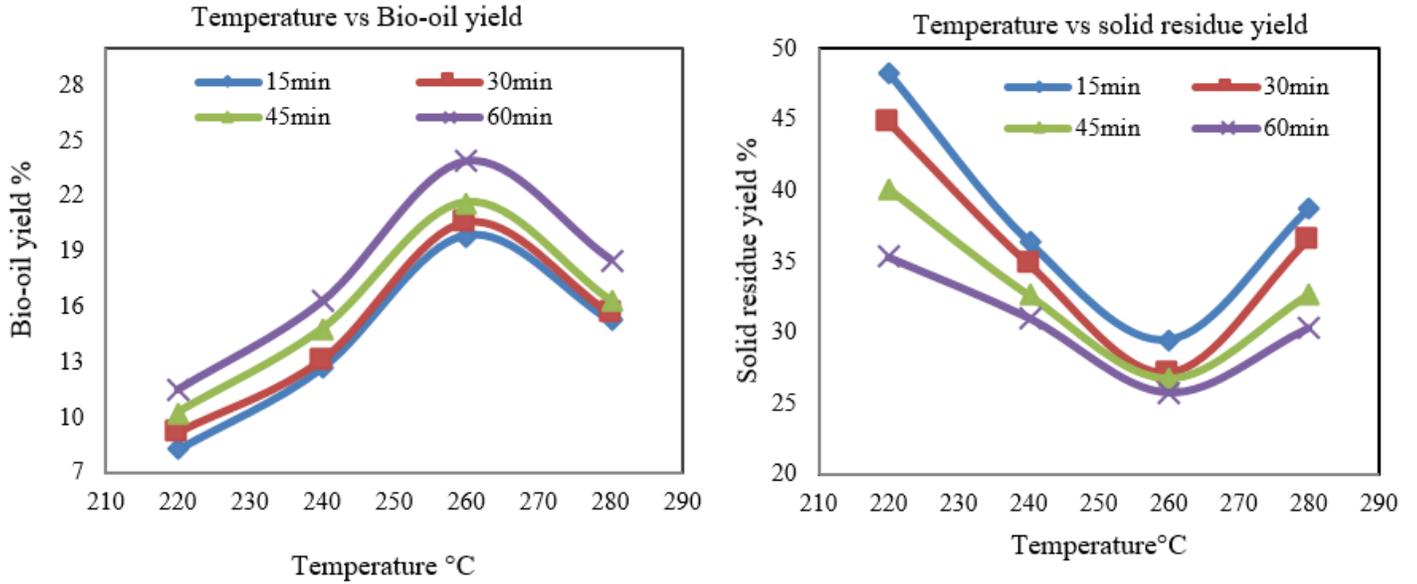


Figure 4

Bio-oil and solid residue yield using different temperatures with catalyst and without co-solvent

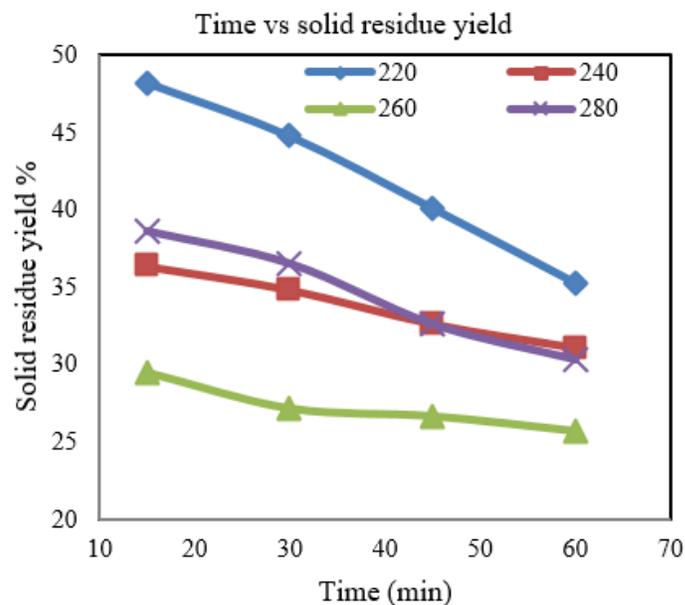
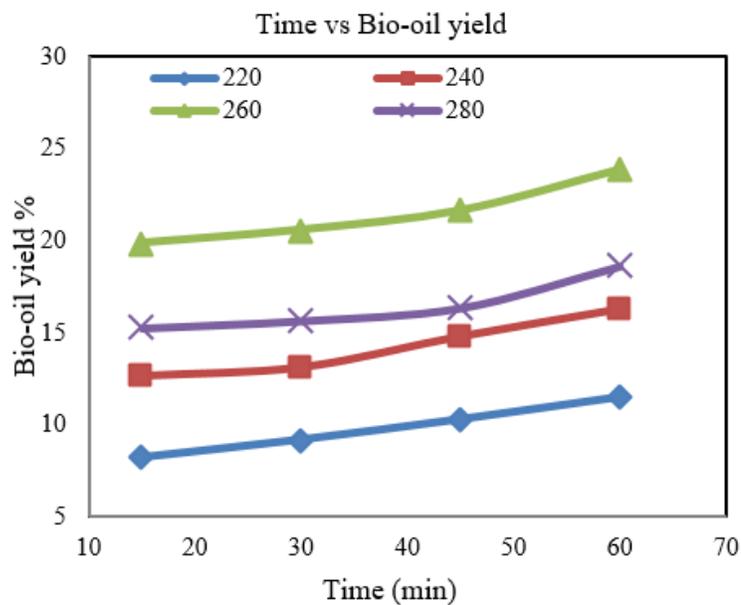


Figure 5

Bio-oil and solid residue yield using different with catalyst and without co-solvent

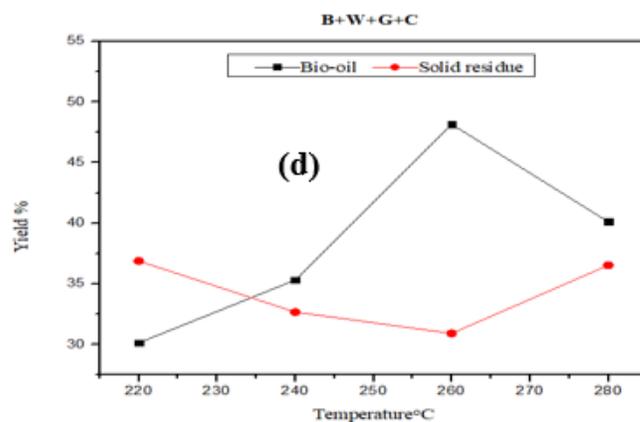
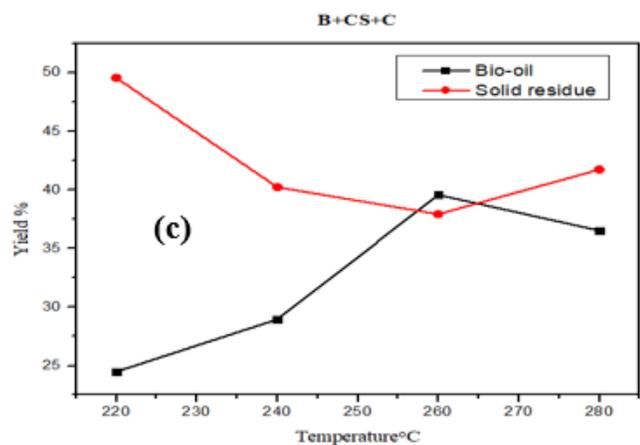
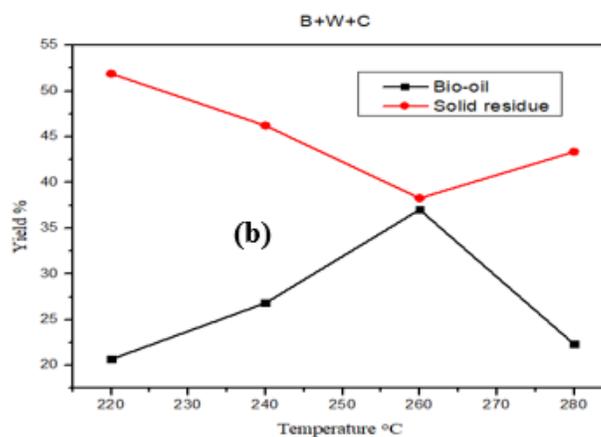
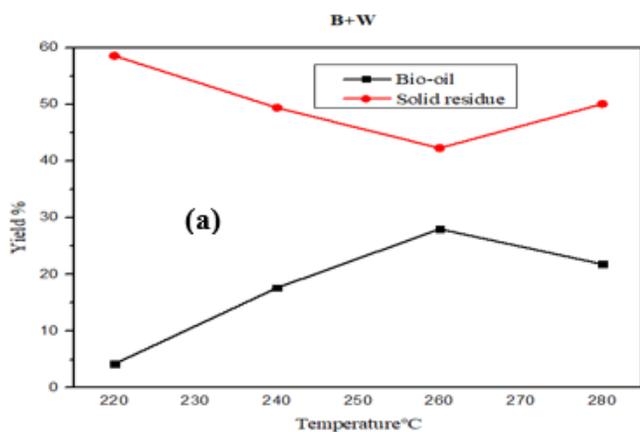


Figure 6

yields of Bio-oil and solid residue with varying process parameters (a) without catalyst and glycerol (b) with catalyst and without glycerol (c) with catalyst and without water (d) with catalyst, water and glycerol.

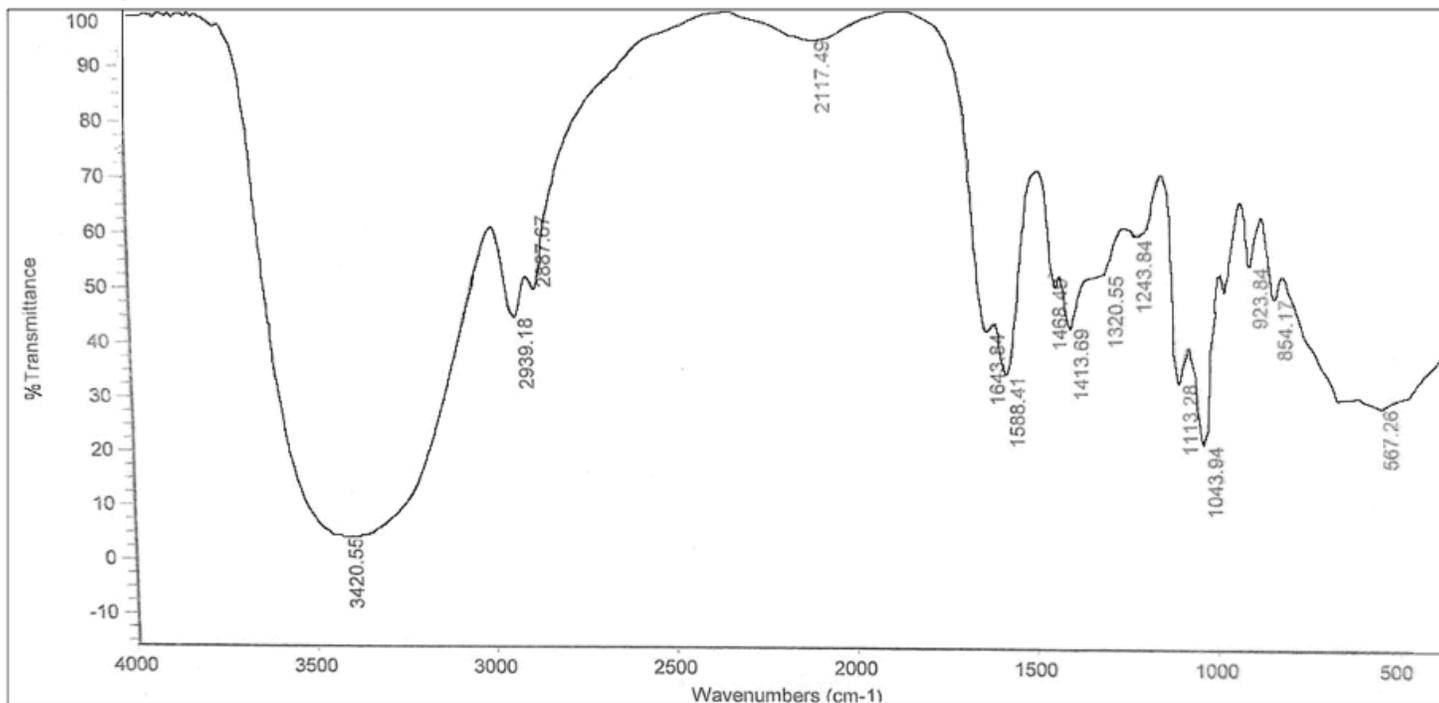


Figure 7

FTIR spectra of bio-crude under optimum conditions

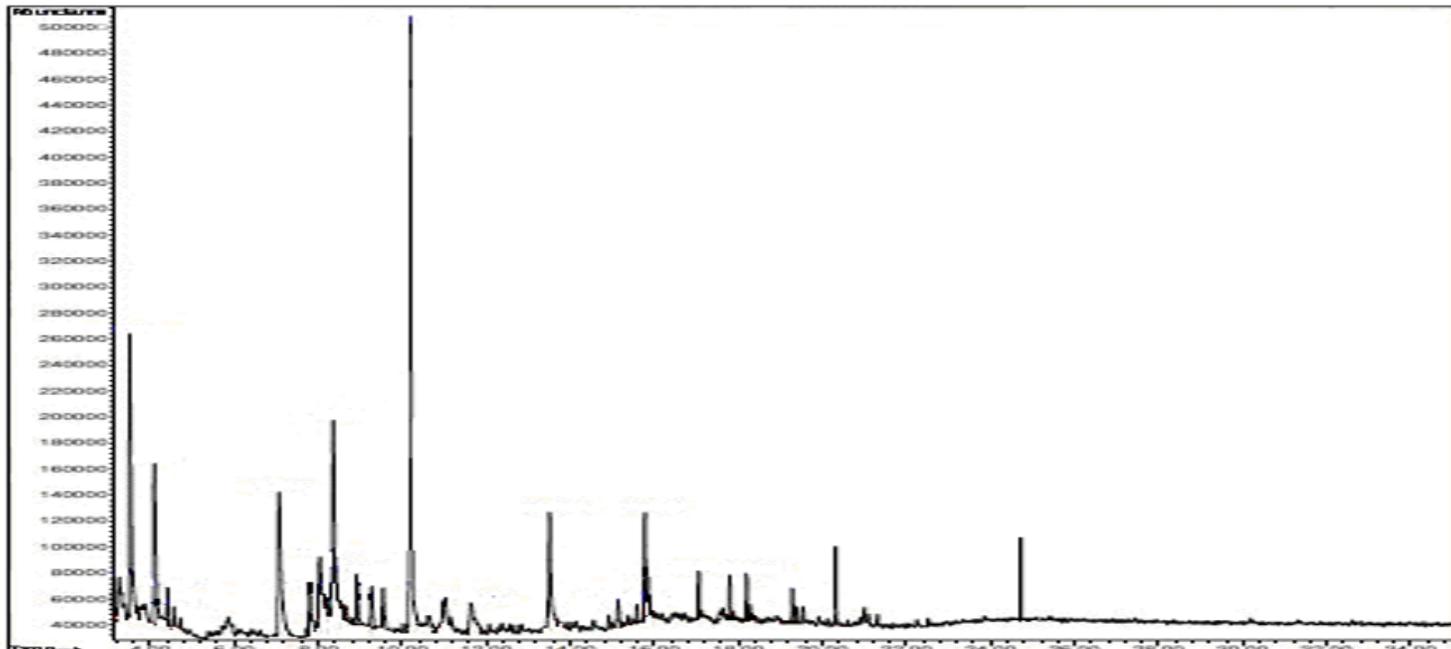


Figure 8

Chromatogram of bio-crude at optimum condition

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