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Catalytic Hydrothermal Liquefaction of Castor Residue: Effect on Product Yield and Distribution of Liquid Product

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ABSTRACT

Castor plant (*Ricinus communis*) is an evergreen perennial shrub, typically found in India, Eastern Africa, and tropical regions. Hydrothermal liquefaction (HTL) of castor plant residue (leaves and stem) was performed at different operating temperatures (260, 280, 300°C) at a residence time of 60 min in the presence of alkali catalysts (KOH, K₂CO₃). The maximum total bio-oil yield (TBO) of ca. 21.2 wt.% was obtained at 300°C, 60 min and in the presence of 0.5 M K₂CO₃. The obtained bio-products (bio-oil, bio-char) have been analyzed using the Elemental analysis (CHNS), Gas Chromatography-Mass Spectrometry (GC-MS), Fourier transform infrared spectroscopy (FT-IR), Proton Nuclear magnetic resonance spectroscopy (¹H NMR), X-ray diffraction (XRD), and Scanning electron microscopy (SEM). The major compounds identified in bio-oil by GC-MS were phenols, aromatic hydrocarbons, N-contained compounds, aldehydes, ketones, amides, alcohols, and acids.

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1. Introduction

In 2018, fossil fuels such as natural gas, oil, and coal contributed 24.0, 34.0, and 27.2% respectively in the World's primary energy consumption (BP Statistical Review of World Energy, 2019). The increase in fossil fuels demand, changes in climate, and decreases in crude-oil reserves have shifted the global dependence on fossil-based energy resources to renewable energy production technologies. The drawbacks of first-generation biofuels associated with its availability and competition with the food vs. fuel are replaced by second-generation biofuels. Lignocellulosic biomass, a second-generation feedstock is abundant in nature, and carbon-neutral renewable energy resource can be used for the production of biofuels, bio-chemicals and value-added products. Woody biomass, agricultural residues and by-products, organic wastes, energy grown plantations, variety of grass are the different sources of biomass (Kaur et al., 2019a).

The different conversion routes of biomass to biofuels are biochemical and thermochemical. The biochemical pathway includes the enzymatic transformation of hemicellulose and cellulose to sugars and subsequent fermentation to bioethanol. Thermochemical process(es) involves the heating of biomass in the presence/absence of air or oxygen and categorized are as Combustion, Gasification, Pyrolysis, and Liquefaction (Kaur et al., 2015). Hydrothermal liquefaction (HTL)

conversion process includes the conversion of biomass in subcritical water to hydrocarbons (Peterson *et al.*, 2008), and the obtained liquid product is referred as biocrude or bio-oil. HTL gained more attention as compared to other thermal conversion technologies due to its advantages. One of significant advantages of hydrothermal liquefaction is that it prevents the need for drying of the feedstocks for producing biocrude (Xiu and Shahbazi, 2012).

Castor plant (*Ricinus communis*) is an evergreen plant from Euphorbiaceae family and genus *Ricinus*. It is mainly grown in India, Eastern Africa, tropical and subtropical regions. Castor plant is widely found along stream banks, distributed areas, river beds, bottomlands by self-pollination. The plant is divided into three parts: seeds, stem, and leaves. Globally, the maximum production of castor seed is in India and India ranks first with production of 22,36,000 MT seeds in 2016 (Comprehensive Castor Oil Report, 2017). The oil obtained from seeds has many industrial and medicinal applications. The other parts of the plant (stem and leaves) contribute more than 50 % of residue generation based on per ton of castor plant (Bateni and Karimi, 2016). The research on each part of the castor plant was performed as castor oil is used for biodiesel production by different researchers (Berman et al., 2011; Canoira et al., 2010; Panwar et al., 2010; Pradhan et al., 2012) and they conclude that reduction of castor oil viscosity from 226.82cS to 8.50cS

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at 38°C is required to make it available a transportation fuel. The various parameters that affect the yield of fatty acid methyl esters are catalyst concentration and methanol to oil molar ratio. A positive interaction was observed among the effect of catalyst concentration, methanol to oil molar ratio and reaction temperature. The kinetic study on castor bean presscake was reported by different researchers (Santos et al., 2015; Thiagarajan, 2016). The study reported on pyrolysis of castor bean cake concludes that the highest bio-oil yield of 63% was obtained at reaction temperature of 400°C for 60 min (Aldobouni et al., 2015). The kinetic study on castor residue (leaves and stems) was reported first time to understand the pyrolytic characteristics, kinetics and thermodynamic properties of feedstock (Kaur et al., 2018). This study concludes that the obtained kinetic and thermodynamic results can be useful input for the design of pyrolytic process. Overall, it was found that the castor residue has significant energy so that it can be used as a feedstock for bioenergy applications. Hydrothermal liquefaction of castor residue at different reaction temperature (260, 280, 300°C) and residence time of 15-90 min in the presence of water was performed. Reaction temperature is the main parameter that affects the total bio-oil (TBO) yield and the optimum residence time based on maximum TBO yield (15.8 wt.%) was 60 min (Kaur et al., 2019b). Based on the above conclusions, the optimum residence time of 60 min was used in the present study to understand the effect of temperature and catalyst on product yield.

To best of our knowledge, no study has been reported yet on catalytic hydrothermal liquefaction of castor residue (leaves and stems) in open literature. With the same aim, hydrothermal liquefaction of castor residue was carried out at 260, 280, 300°C at residence time of 60 mins in the presence of alkali catalyst (KOH and K_2CO_3). Alkali based homogenous catalysts (0.5M KOH, 0.5M K_2CO_3) were used to know the effect of catalyst on product yield and formation of compounds. The obtained bio-products were analyzed by Elemental analysis (CHNS), Gas Chromatography-Mass Spectrometry (GC-MS), Fourier transform infrared spectroscopy (FT-IR), Proton Nuclear magnetic resonance spectroscopy (^1H NMR), X-ray diffraction (XRD), and Scanning electron microscopy (SEM).

2. Material and Methods

2.1 Raw material

The castor residue used in this work was collected from the boundary of Dr B R Ambedkar National Institute of Technology (31.3962° N, 75.5354° E), Jalandhar, Punjab. After crushing and sieve shaking, the obtained fine powder was used for further analysis. The catalyst (0.5M KOH, 0.5M K_2CO_3) was prepared in lab. Proximate analysis, elemental analysis, and component analysis of castor residue was performed, and the methods used were explained in our previous study (Kaur et al., 2018). HHV of castor residue and bioproducts were calculated using Dulong's formula:

$$\text{Heating value (MJ/kg)} = 0.338 C + 1.428 (H - O/8) + 0.095 S \quad (1)$$

2.2 Apparatus and experimental procedure

Hydrothermal liquefaction experiments were conducted in a high-pressure batch autoclave (Parr reactor) at different reaction conditions in the presence of alkaline catalysts (KOH, K_2CO_3). In each catalytic hydrothermal experiment, the reactor was loaded with castor residue and alkaline solutions with a ratio of 1:6 (by weight). Then the reactor was sealed and purged with nitrogen for atleast 5 times to remove the inside air. The reactants were then agitated vertically with ≈ 200 rpm using vertical magnetic stirrer. The reactor was then heated upto desired temperature (260, 280, 300 °C) for residence time of 60 min. The reactor was then left to cool down to the room temperature.

2.3 Extraction of liquid products and analysis

After cooling of the reactor, gaseous products were vented out. The liquid and solid products were then separated using vacuum filtration. Diethyl ether of equal quantity was then added to liquid portion for its recovery. Phase separation of liquid product in organic and aqueous fraction was carried out in a separating funnel. The obtained organic or ethereal fraction was then dried over anhydrous sodium sulfate to remove the moisture or water content. Diethyl ether was then extracted using rotary vacuum evaporator under reduced pressure. The obtained fraction was then designated as bio-oil 1 or BO1. The aqueous phase is a mixture of water-soluble oxygenated hydrocarbons, designated as others and water-soluble oxygenated hydrocarbons (WSH). The acetone soluble fraction was then extracted out from solid product in soxhlet apparatus using acetone as solvent until the solvent in thimble become colorless. The

liquid fraction obtained after evaporating the acetone under reduced pressure was weighed and termed as bio-oil 2 or BO2. The insoluble acetone fraction was then dried at 105°C and designated as bio-char or BC. The mass balance equations used in this procedure are:

$$\text{Conversion, \%} = \frac{W_{\text{feed}} - W_{\text{bio-char}}}{W_{\text{feed}}} \times 100 \quad (1)$$

$$\text{Bio - oil 1 or BO1 yield} = \frac{W_{\text{ether-soluble}}}{W_{\text{feed}}} \times 100 \quad (2)$$

$$\text{Bio - oil 2 or BO2 yield, wt. \%} = \frac{W_{\text{acetone-soluble}}}{W_{\text{feed}}} \times 100 \quad (3)$$

$$\text{Bio - char or BC yield, wt. \%} = \frac{W_{\text{bio-char}}}{W_{\text{feed}}} \times 100 \quad (4)$$

$$\text{Gas yield, wt. \%} = \frac{R1 - R2}{R3} \times 100 \quad (5)$$

$$\text{Other yield, wt. \%} = 100 - (\text{bio - oil 1} + \text{bio - oil 2} + \text{bio - char} + \text{gas}) \quad (6)$$

W_{feed} : is the weight of feed; $W_{\text{bio-char}}$: is the weight of bio-char; $W_{\text{ether-soluble}}$: is the weight of ether soluble bio-oil or BO1; $W_{\text{acetone-soluble}}$: is the weight of acetone soluble bio-oil or BO2. R1 = Initial weight of the reactor + feed + solvent before HTL; R2 = Final weight of the reactor + feed + solvent after HTL. R3 = Amount of feed taken (g) + Amount of solvent added (g).

Castor residue was analyzed using FT-IR, XRD, and SEM. The liquid fraction is the most desirable product in the hydrothermal liquefaction, and the optimum conditions are where maximum amount of total bio-oil was attained. Further, the bio-products (bio-oil and bio-char) obtained at the particular optimum conditions were analyzed using FT-IR, GC-MS, ^1H NMR, Elemental analysis, SEM, and XRD.

3. Results and discussions

3.1 Feedstock analysis

Castor residue has carbon, hydrogen, nitrogen, and oxygen content of 43.59 wt.%, 5.56 wt.%, 4.69 wt.%, 46.16 wt.% respectively. Moisture, ash, fixed carbon and volatile matter content present in castor residue was 11.14 wt.%, 5.40 wt.%, 9.16 wt.%, and 74.30 wt.% respectively. The high heating value of castor residue calculated using Dulong's formula was 14.43 MJ/kg. Castor residue is lignocellulosic biomass and has cellulose, hemicellulose and lignin content of 38.42 wt.%, 22.40 wt.% and 20.20 wt.% respectively. Extractives in the form of gum, resins, and proteins, etc are also part of castor residue and observed as 16.40 wt.%.

3.2 HTL products yields

Table 1 depicts the product distribution of castor residue obtained after catalytic hydrothermal liquefaction. Equations (2) to (7) were used to calculate the yield of the product. Temperature and catalysts affect the total bio-oil yield and conversion. The trend of conversion for K_2CO_3 was first decreases at 280°C and then increases with further increase in temperature (300°C) was observed and highest conversion of 85.0 wt.% was found at 300°C in the presence of K_2CO_3 . The conversion for KOH varies from 68.6, 77.6, 82.8 wt.% for 260, 280, and 300°C respectively. It was observed that the maximum total bio-oil yield of ca. 21.2 wt.% was observed at 300°C in the presence of K_2CO_3 . The maximum total bio-oil yield of ca. 12.2 wt.% was obtained at 300°C when KOH is used as catalyst. It was observed that the TBO yield was more in K_2CO_3 means it is more effective catalyst as compared to KOH. Similar to this, HTL of wheat husk was conducted in the presence of both alkali catalysts (KOH and K_2CO_3) at 280°C for 15 min, and similar conclusion was made that the K_2CO_3 is more reactive than KOH (Singh et al., 2013). The maximum total bio-oil yield of 30 and 31 wt.% was obtained in the presence of KOH and K_2CO_3 respectively. The other studies (Bhaskar et al., 2008; Karagoz et al., 2005; Singh et al., 2015) reported in literature proved the same reactivity of alkali catalysis. The possible reason for the behavior of alkali salts during sub-critical process is they react and form their bases and bicarbonates. Bicarbonates may act as secondary catalyst and enhance the product yield (Karagoz et al., 2005). The effect of alkali catalysts on total bio-oil yield was observed by comparing the values with our

previously reported study (Kaur et al., 2019b) where water was used as catalyst, and it was concluded the 0.5 M K_2CO_3 was the most reactive catalyst. The major fraction of others or WSH fraction was observed ranging from 50.7-65.7 and 49.7-56.7 wt.% for KOH and K_2CO_3 respectively and possibly derived from carbohydrates present in castor residue. The biochar yield varies between 17.2-31.4 wt.% and 15.0-30.8 wt.% for KOH and K_2CO_3 respectively. An increase in the TBO yield with increase in temperature was due to the decomposition of solids and condensation of gases (Liu and Zhang, 2008).

Table 1: Product distributions, wt.% of castor residue from catalytic hydrothermal liquefaction at different reaction conditions.

Sample Code	Bio-oils		Total Bio-oil	Gases	Bio-char	Other yield	Conversion
	Bio-oil 1	Bio-oil 2					
260-60 0.5M KOH	7.2	2.4	9.6	8.3	31.4	50.7	68.6
280-60 0.5 M KOH	8.8	1.2	10	5.9	22.4	61.7	77.6
300-60 0.5M KOH	8.6	3.6	12.2	4.9	17.2	65.7	82.8
260-60 0.5M K_2CO_3	15.2	0.2	15.4	7.5	27.4	49.7	72.6
280-60 0.5M K_2CO_3	13.8	0.2	14	10.0	30.8	45.2	69.2
300-60 0.5M K_2CO_3	20.8	0.4	21.2	7.1	15.0	56.7	85.0

3.3 Feedstock and Product characterization

3.3.1 GC-MS analysis of BO1

Table 2 represents the compounds obtained in BO1 of castor residue from catalytic hydrothermal liquefaction at 300°C for 60 mins in the presence of 0.5 M KOH and K_2CO_3 . NIST mass spectral database was used for the identification of compounds. The chemical compounds of bio-oil were identified as phenolics, aromatic hydrocarbons, N-contained compounds, aldehydes, ketones, amides, alcohols, and acids. It was observed that the use of catalyst affects the formation of compounds. A maximum area % 28.22 of compound 5-Bromo-4-oxo-4,5,6,7-tetrahydrobenzofurazan was observed when KOH was used as catalyst. Compounds such as Stigmasterol, γ -Sitosterol, Isophytol, Phytol, Eicosane, γ -Tocopherol, Butylated Hydroxytoluene, 2-Pentadecanone, 6,10,14-trimethyl- was observed in both catalysts but the area % of the similar compounds was quite high in case of KOH as compared to K_2CO_3 . The formation of compounds 2-Cyclopenten-1-one, Phenol, p-Cresol, Benzene, 3-Methoxybenzyl alcohol, Indole was observed when HTL of castor residue was done in the presence of K_2CO_3 . It was observed that the area % of phenolic compounds were more and can be used as a feedstock in chemical and pharmaceutical industry or as a substitute for bio-phenolic resins etc.

3.3.2 FT-IR analysis of castor residue and BO1

Figure 1 shows the FT-IR analysis of castor residue and BO1 obtained after catalytic HTL of castor residue at 300°C. The absorption peak ranges between 3200-3600 cm^{-1} is due to N-H and O-H stretching represents the presence of amides/amines, alcohols and phenols. The C-H stretching vibrations at 2800 - 3000 cm^{-1} indicates the presence of alkanes (Aysu, 2014). The C=O stretching vibrations between 1680-1800 cm^{-1} indicate the presence of ketones, carboxylic acids, and aldehydes. Besides, the C=C stretching peak between 1400-1600 cm^{-1} suggests the presence of aromatics, and the substituted aromatic groups are observed at 675-900 cm^{-1} (Guo et al., 2008). The C-H deformation vibrations between 1360-1460 cm^{-1} show the presence of alkane group. The vibrations in the region 1020 - 1300 cm^{-1} were assigned to C-N stretching vibrations which are possibly due to aliphatic amines. The significant difference between the vibrations of castor residue and BO1 is the absence of peak in the range of 1680-1800 cm^{-1} in castor residue, while the remaining vibrations were similar in all samples. Comparing the FT-IR analysis obtained under different catalytic conditions (KOH and K_2CO_3), it was noticed that the almost same functional groups were present in both BO1 but at different relative intensity.

Table 2: Major compounds identified in BO1, Area, % of castor residue from catalytic hydrothermal liquefaction using GC-MS.

RT	Library/ID	BO1 300-60 0.5M KOH	BO1 300-60 0.5M K_2CO_3
3.63	Cyclopentanone, 2-methyl-	-	3.42
4.36	1-Butylpyrrolidine	-	1.36
4.77	Cyclopentanone, 2-ethyl-	-	1.03
5.64	Phenol	-	8.71
6.27	Pyridine-D5-	-	0.74
6.28	N-.beta.-Hydroxyethylpyrrolidine	1.71	-
6.32	Pyridine, 5-ethyl-2-methyl-	-	0.70
6.42	2-Cyclopenten-1-one, 2,3-dimethyl-	-	3.02
6.79	1-Butanamine, 2-methyl-N-(2-methylbutylidene)-	-	0.61
7.14	p-Cresol	-	1.80
7.51	2-Cyclopenten-1-one, 3,4,4-trimethyl-	-	7.22
7.59	Phenol, 2-methoxy-	-	2.61
8.02	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	-	1.18
8.85	1,3-Benzenediamine, 4-methoxy-	-	0.65
8.99	Creosol	-	0.60
9.22	Benzene, 1-methoxy-4-methyl-	-	1.46
9.50	3-Methoxybenzyl alcohol	-	0.48
9.77	Phenol, 3-ethyl-	-	0.52
9.88	2-Ethyl-3,5-dimethylpyridine	-	0.80
11.47	Quinoline, 1,2,3,4-tetrahydro-	-	0.63
12.36	Indole	-	2.36
14.49	1H-Indole, 4-methyl-	-	1.52
17.77	Butylated Hydroxytoluene	8.39	7.00
24.92	2-Pentadecanone, 6,10, 14-trimethyl-	1.99	0.81
26.99	Isophytol	4.39	1.48
29.85	Phytol	4.61	4.50
41.72	Eicosane	3.33	1.40
43.06	γ -Tocopherol	2.29	1.67
44.04	Vitamin E	5.17	2.00
45.57	Stigmasterol	6.00	2.23
46.43	γ -Sitosterol	16.29	5.40
46.55	2-Ethylacridine	-	1.20
46.93	1,4-Bis (trimethylsilyl) benzene	-	1.50
47.37	5-Bromo-4-oxo-4,5,6,7-tetrahydrobenzofurazan	28.22	-
Total		82.39	70.61

Figure 1: FT-IR analysis of castor residue and BO1 obtained after catalytic HTL of castor residue

3.3.3 Proton NMR analysis of BO1

Figure 2 shows the ^1H NMR analysis of BO1 obtained at catalytic HTL of castor residue at 300 °C. Proton NMR provides information of types of proton present in the compound by divulging the basic structure of the complex organic species present in BO (Dhyani et al., 2017). The spectra 0.5-1.5 ppm represents the protons on aliphatic carbon atoms at least two bonds away from C=C or heteroatom (Singh et al., 2015b). It was observed that more aliphatic protons for the case of KOH (68.73%) as compared to K_2CO_3 . The next region 1.5-3.0 ppm corresponds to protons on aliphatic carbon atoms may be bonded to a C=C double bond or heteroatom. The protons in this region were less in KOH as compared to K_2CO_3 (28.01%). In the next zone, 3.0-4.7 ppm more protons were observed in the case of K_2CO_3 (8.01%), represents the protons on carbon atom next to an aliphatic ether or alcohol or a methylene group that joins two aromatic rings. The region between 4.5-6.0 ppm depicts the presence of aromatic ether protons, i.e., lignin derived phenols. The percentage of protons in this region is almost similar for both KOH and K_2CO_3 catalysts. The region of spectrum 6.0-8.5 ppm corresponds to aromatics, and more was observed in the case of K_2CO_3 (5.45%).

Figure 2: ^1H NMR analysis of BO1 obtained after catalytic HTL of castor residue

3.3.4 Elemental analysis of BO1

Table 3 represents the elemental analysis of bio-oil 1 obtained for both HTL of castor residue using KOH and K_2CO_3 catalyst. BO1 have carbon content of 62.20 wt.% and 62.80 wt.% for KOH and K_2CO_3 respectively. The oxygen content of bio-oil1 is less in the case of K_2CO_3 as compared to KOH. Reactions such as dehydrogenation ($-\text{H}_2$), decarbonylation ($-\text{CO}$) and decarboxylation ($-\text{COO}$) were involved in

Elements	BO1 300-60 0.5M KOH	BO1 300-60 0.5M K_2CO_3
Carbon, wt. %	62.27	62.80
Hydrogen, wt. %	10.92	11.73
Nitrogen, wt. %	2.22	2.62
Oxygen, wt. %	24.59	22.85
HHV, MJ/kg	32.27	33.91

the liquefaction process helps to reduce the oxygen content of BO1. The heating value of BO1 for KOH and K_2CO_3 are 32.27 and 33.91 MJ/kg respectively. The reduction in wt.% of nitrogen in bio-oil1 was observed as compared to castor residue. Further denitrogenation and deoxygenation will be required to make this bio-oils more effective so that it can be used for transportation purposes too.

3.3.5 Bio-char analysis

3.3.5.1 Elemental analysis of Bio-char

The elemental analysis of bio-char obtained after catalytic HTL of castor residue at 300 °C at 60 min was done. The carbon, hydrogen, nitrogen, and oxygen content of bio-char obtained using KOH were 59.92, 6.35, 1.02 and 32.71 wt.% respectively. The elements present in bio-char obtained using K_2CO_3 were 59.97 wt.% of C, 6.81 wt.% of H, 1.61 wt.% of N and 31.60 wt.% of O. The HHV of bio-char calculated using Dulong's formula were 23.50 and 24.37 MJ/kg for KOH and K_2CO_3 respectively. It was observed that the nitrogen content of bio-char is less as compared to castor residue.

3.3.5.2 XRD analysis of Bio-char

The XRD patterns of feedstock and bio-char were shown in Figure 3. The change in cellulose crystalline structures was observed by interrupting hydrogen bonding of cellulose chains (Mosier et al., 2005). The X-ray diffraction pattern of raw material showed two distinct peaks at $2\theta = 15^\circ$ and 22° of cellulose. After catalytic HTL of castor residue, the shift of peaks ($2\theta = 29^\circ$) towards its higher value was observed and showed the formation of hydrochar from cellulose and lignin present in lignocellulosic biomass. The change in peak intensity of bio-char for K_2CO_3 and KOH was may be due to the difference in component decomposition temperature, i.e., for cellulose starts at 200-250°C (Sakaki et al., 1996).

Figure 3: XRD patterns of Bio-char obtained after catalytic HTL of castor residue

3.3.5.3 SEM analysis of Bio-char

Change in the structure was observed in the micrographs of SEM as shown in Figure 4. The castor residue {Figure 4 (a)} as feedstock is a lumpy solid, dense matrix having strongly bounded stripes. The bio-char {Figure 4 (b-c)} obtained using catalytic HTL (0.5 M KOH and 0.5 M K_2CO_3) shows the formation of agglomerates appeared on the surface may be due to cross-linking caused by dehydration between molecules of cellulose and hemicellulose (Sun and Li, 2004).

Figure 4: SEM micrographs of Bio-char obtained after catalytic HTL of castor residue

4. Conclusions

Catalytic hydrothermal liquefaction of castor residue was performed in the presence of 0.5 M KOH and K_2CO_3 . The maximum total bio-oil yield, ca. 21.2 wt.% was obtained for 0.5 M K_2CO_3 as compared to 0.5 M KOH. It was observed that the use of alkali catalyst (0.5 M K_2CO_3) enhances the total bio-oil yield. The formation of phenolic compounds was confirmed by GCMS, FT-IR, and NMR and made it promising material to be used as a phenol substitute in bio-phenolic resins. The HHV of BO1 for KOH and K_2CO_3 were 32.27 and 33.91 MJ/kg respectively while for bio-char it was 23.50 and 24.37 MJ/kg for KOH and K_2CO_3 respectively. The HHV of bio-char was more as compared to feedstock which makes it promising feedstock to be used as solid fuel in boilers, for the production of carbon nanotubes and activated carbon as well.

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References

- Aldobouni, I.A., Fadhil, A.B., Saied, I.K., 2015. Conversion of de-oiled castor seed cake into bio-oil and carbon adsorbents. *Energy Sources, Part A Recover. Util. Environ. Eff.* 37, 2617–2624.
- Aysu, T., 2014. Catalytic effects of ferric chloride and sodium hydroxide on supercritical liquefaction of thistle (*Cirsium yildizianum*). *J. Supercrit. Fluids* 95, 298–317. doi:10.1016/j.supflu.2014.09.024
- Bateni, H., Karimi, K., 2016. Biodiesel production from castor plant integrating ethanol production via a biorefinery approach. *Chem. Eng. Res. Des.* 107, 4–12. doi:10.1016/j.cherd.2015.08.014
- Berman, P., Nizri, S., Wiesman, Z., 2011. Castor oil biodiesel and its blends as alternative fuel. *Biomass and Bioenergy* 35, 2861–2866. doi:10.1016/j.biombioe.2011.03.024
- Bhaskar, T., Sera, A., Muto, A., Sakata, Y., 2008. Hydrothermal upgrading of wood biomass: influence of the addition of K_2CO_3 and cellulose/lignin ratio. *Fuel* 87, 2236–2242.
- BP Statistical Review of World Energy. Online Available at: <https://www.bp.com/dam/global/corporate/pdfs/energy-economics>. Accessed on 23rd August 2019.
- Canoira, L., García Galeán, J., Alcántara, R., Lapuerta, M., García-Contreras, R., 2010. Fatty acid methyl esters (FAMES) from castor oil: Production process assessment and synergistic effects in its properties. *Renew. Energy* 35, 208–217. doi:10.1016/j.renene.2009.05.006
- Comprehensive Castor Oil Report [WWW document] d.g. URL <http://www.castoroil.in/reference/report/report.html>. Accessed on 25 July 2017.
- Dhyani, V., Awasthi, A., Kumar, J., Bhaskar, T., 2017. Pyrolysis of Sorghum straw: Effect of temperature and reaction environment on the product behavior. *J. Energy Environ. Sustain.* 4, 64–69.
- Guo, S., Wu, L., Wang, C., Li, J., Yang, Z., 2008. Direct conversion of sunflower shells to alkanes and aromatic compounds. *Energy & Fuels* 22, 3517–3522.
- Karag??z, S., Bhaskar, T., Muto, A., Sakata, Y., Oshiki, T., Kishimoto, T., 2005. Low-temperature catalytic hydrothermal treatment of wood biomass: Analysis of liquid products. *Chem. Eng. J.* 108, 127–137. doi:10.1016/j.ccej.2005.01.007
- Kaur, R., Gera, P., Jha, M.K., 2015. Study on Effects of Different Operating Parameters on the Pyrolysis of Biomass: A Review. *J. Biofuels Bioenergy* 1, 135–147.
- Kaur, R., Gera, P., Jha, M.K., Bhaskar, T., 2019a. Thermochemical Route for Biohydrogen Production, *Biohydrogen*. doi:10.1016/b978-0-444-64203-5.00008-3
- Kaur, R., Gera, P., Jha, M.K., Bhaskar, T., 2019b. Reaction parameters effect on hydrothermal liquefaction of castor (*Ricinus Communis*) residue for energy and valuable hydrocarbons recovery. *Renew. Energy* 141, 1026–1041. doi:10.1016/j.renene.2019.04.064
- Kaur, R., Gera, P., Jha, M.K., Bhaskar, T., 2018. Pyrolysis kinetics and thermodynamic parameters of castor (*Ricinus communis*) residue using thermogravimetric analysis. *Bioresour. Technol.* 250, 422–428. doi:10.1016/j.biortech.2017.11.077
- Liu, Z., Zhang, F.S., 2008. Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks. *Energy Convers. Manag.* 49, 3498–3504. doi:10.1016/j.enconman.2008.08.009
- Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M., Ladisch, M., 2005. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour. Technol.* 96, 673–686. doi:10.1016/j.biortech.2004.06.025
- Panwar, N.L., Shrirame, H.Y., Bamniya, B.R., 2010. CO 2 mitigation potential from biodiesel of castor seed oil in Indian context. *Clean Technol. Environ. Policy* 12, 579–582.
- Peterson, A.A., Vogel, F., Lachance, R.P., Fröling, M., Antal, Jr., M.J., Tester, J.W., 2008. Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy Environ. Sci.* 1, 32. doi:10.1039/b810100k
- Pradhan, S., Madankar, C.S., Mohanty, P., Naik, S.N., 2012. Optimization of reactive extraction of castor seed to produce biodiesel using response surface methodology. *Fuel* 97, 848–855. doi:10.1016/j.fuel.2012.02.052
- Sakaki, T., Shibata, M., Miki, T., Hirose, H., Hayashi, N., 1996. Reaction model of cellulose decomposition in near-critical water and fermentation of products. *Bioresour. Technol.* 58, 197–202.
- Santos, N.A. V, Magriotis, Z.M., Saczk, A.A., Fa ssio, G.T.A., Vieira, S.S., 2015. Kinetic study of pyrolysis of castor beans (*Ricinus communis* L.) presscake: an alternative use for solid waste arising from the biodiesel production. *Energy & Fuels* 29, 2351–2357.
- Singh, R., Balagurumurthy, B., Prakash, A., Bhaskar, T., 2015a. Catalytic hydrothermal liquefaction of water hyacinth. *Bioresour. Technol.* 178, 157–165. doi:10.1016/j.biortech.2014.08.119
- Singh, R., Bhaskar, T., Dora, S., Balagurumurthy, B., 2013. Catalytic hydrothermal upgrading of wheat husk. *Bioresour. Technol.* 149, 446–451. doi:10.1016/j.biortech.2013.09.092
- Singh, R., Chaudhary, K., Biswas, B., Balagurumurthy, B., Bhaskar, T., 2015b. Hydrothermal liquefaction of rice straw: Effect of reaction environment. *J. Supercrit. Fluids* 104, 70–75. doi:10.1016/j.supflu.2015.05.027
- Sun, X., Li, Y., 2004. Colloidal Carbon Spheres and Their Core/Shell Structures with Noble-Metal Nanoparticles. *Angew. Chemie - Int. Ed.* 43, 597–601. doi:10.1002/anie.200352386
- Thiagarajan, J., 2016. Thermogravimetric and Decomposition analysis of *Jatropha*, Castor and *Pongamia* Deoiled seed cakes. *Int. J. Innov. Eng. Technol.* 7, 417–425.
- Xiu, S., Shahbazi, A., 2012. Bio-oil production and upgrading research: A review. *Renew. Sustain. Energy Rev.* 16, 4406–4414. doi:10.1016/j.rser.2012.04.028