

Article

Hydrothermal Liquefaction of Rice Straw Using Methanol as Co-Solvent

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Received: 2 April 2020; Accepted: 28 April 2020; Published: 21 May 2020



Abstract: Hydrothermal liquefaction (HTL) is a promising thermochemical process to treat wet feedstocks and convert them to chemicals and fuels. In this study, the effects of final temperature (300, 325, and 350 °C), reaction time (30 and 60 min), rice-straw-to-water ratio (1:1, 1:5, 1:10, and 1:15 (wt./wt.)), methanol-to-water ratio (0:100, 25:75, 50:50, and 75:25 (vol./vol.)), and alkali catalysts (KOH, NaOH, and K₂CO₃) on product yields, composition of bio-crude, higher heating value (HHV) of bio-crude and bio-char, and energy recovery on HTL of rice straw are investigated. At the optimal processing condition corresponding to the final temperature of 300 °C, 60 min reaction time, and rice-straw-to-water ratio of 1:10 at a final pressure of 18 MPa, the bio-crude yield was 12.3 wt.% with low oxygen content (14.2 wt.%), high HHV (35.3 MJ/kg), and good energy recovery (36%). The addition of methanol as co-solvent to water at 50:50 vol./vol.% improved the yield of bio-crude up to 36.8 wt.%. The selectivity to phenolic compounds was high (49%–58%) when only water was used as the solvent, while the addition of methanol reduced the selectivity to phenolics (13%–22%), and improved the selectivity to methyl esters (51%–73%), possibly due to esterification reactions. The addition of KOH further improved the yield of bio-crude to 40 wt.% in an equal composition of methanol:water at the optimal condition. The energy-consumption ratio was less than unity for the methanol and catalyst system, suggesting that the process is energetically feasible in the presence of a co-solvent.

Keywords: hydrothermal liquefaction; rice straw; bio-crude; methanol; phenols; esters; energy-consumption ratio

1. Introduction

Rice straw is one of the abundant lignocellulosic agro residues in the world. India is the second largest producer of rice in the world, with 106 million tons per year, and an annual production of roughly 160 million tons of straw [1]. Owing to mechanized farming, open field burning of rice straw and its stubble has become a common scene in India, especially in the state of Punjab, and this has led to severe greenhouse gas emissions and pollution in the major cities [2]. In Asian countries, rice straw is often burnt in the open fields, leading to airborne emissions that are hazardous to living organisms and the environment. This also leads to the killing of small animals in the fields and a decline of biodiversity [1]. Hence, there is increased attention toward conversion of rice straw to valuable products, such as chemicals, fuels, energy, and bio-products.

Thermochemical techniques, such as pyrolysis, gasification, combustion, and hydrothermal liquefaction (HTL), are used to convert biomass into valuable chemicals, liquid fuels and oils, and gaseous fuel (syngas) [3–5]. Among these, HTL is the only processing technique that can handle wet biomass feedstocks with as high as 50 wt.% moisture, to produce high-quality bio-crude. HTL is generally carried out at 200–350 °C and between 5 and 30 MPa [5,6]. High-pressure operation ensures that water from the biomass does not get converted into a gaseous phase, thus saving the energy required for enthalpy of vaporization. HTL is an accelerated version of geological formation of fossil fuels [5]. While the formation of fossil fuels underneath the earth's surface takes many years, HTL yields liquid crude in a minutes-to-hours timeframe [5]. Unlike water at ambient conditions, the physicochemical properties of water at near-critical and supercritical conditions make it an excellent solvent. Owing to the fewer and weaker hydrogen bonds in hot compressed water than in water at ambient conditions, better solubility of organic molecules is achieved due to the low dielectric constant of the medium. Moreover, the high ionic product of water near the critical temperature aids in acid/base-catalyzed ionic reactions [6,7]. HTL bio-crude is superior to pyrolysis bio-oil, especially in terms of low oxygen content, high carbon content, high calorific value, and low moisture content [6].

HTL of a variety of feedstocks, such as pine wood [8,9], corn stalk [10], lignin [11,12], sewage sludge [13], corn stover [14], switch grass [15], *Nannochloropsis* sp. [16,17], and spirulina [17], for the production of bio-crude is reported in the literature. HTL of rice straw has also been investigated in the literature [18–22]. Yuan et al. [18] studied the subcritical and supercritical liquefaction of rice straw with different solvent mixtures such as ethanol–water and 2-propanol–water. They conducted the experiments at different temperatures (260–350 °C) and solvent mixture ratios (1:9 to 5:5), and obtained 39.7 wt.% of bio-crude with 2-propanol:water at 5:5 ratio and 300 °C. Li et al. [19] investigated the HTL of rice straw by using 1,4-dioxane:water mixtures and obtained 57 wt.% bio-crude at 300 °C and equal composition of the solvent and water. Singh et al. [20] investigated the HTL of rice straw in the presence of different gases, such as N₂, O₂, and CO₂, at different temperatures, from 280 to 320 °C, at 15 min residence time, and rice-straw-to-water ratio of 1:6. The maximum bio-crude yield of 17 wt.% was obtained in N₂ ambience. The major components of the bio-crude obtained in the presence of N₂ and CO₂ ambience were phenol, guaiacol, syringol, and their derivatives. Zhou et al. [21] used Cu–Zn–Al catalyst for HTL of rice straw in presence of water–ethanol mixtures and obtained a maximum of 26.8% monomeric phenols in the bio-crude at 300 °C, 30 min, 50:50 vol./vol.% of ethanol:water, and 2 g of catalyst. In another study, glycerol was used as a co-solvent, along with Na₂CO₃ as the homogeneous catalyst in HTL, to produce up to 50 wt.% of bio-crude from rice straw [22]. The prospects of scale-up of HTL technology for continuous processing of feedstocks are outlined in the review by Castello et al. [23].

Supercritical alcohols in HTL of biomass possess many advantages, such as ability of donating hydrogen, better solubility, easier separation of bio-crude from kerogen-like residue, and lower corrosivity. Brand and Kim [24] studied liquefaction of cellulose, xylose, and lignin in supercritical ethanol and showed that the chemical composition of bio-crude from cellulose and xylose were quite distinct from the bio-crudes obtained via fast pyrolysis and HTL under subcritical conditions. Methanol possesses low critical temperature and pressure (239 °C, 8.09 MPa), and has established production routes from coal, natural gas, and biomass. In India, it is projected as the future fuel, with blending at up to 15% in transportation fuels. It is also expected to be available at a competitive price in India, owing to its production from coal via a two-step process involving gasification, followed by catalytic reforming of syngas [25]. Chemically, methanol is a hydrogen donor solvent, and hence, a study on its use to improve the quality of bio-crude assumes importance. This study is novel in the following respects: (1) This is the first study to report the use of methanol as a co-solvent in HTL of rice straw; (2) this study exhaustively evaluates the effect of process conditions such as temperature, reaction time, biomass-to-solvent ratio, solvent composition, and alkali catalysts on the yields and quality of bio-crude from rice straw; and (3) this study reports the energetics of the process, to evaluate the

feasibility at salient operating conditions. The quality metrics include organic composition, elemental analysis and calorific value of bio-crude, and elemental composition of calorific value of bio-char.

2. Experimental

2.1. Materials and Feedstock Characterization

Rice straw was procured locally from a farm in Sullurupeta (13.7009° N, 80.0209° E), Andhra Pradesh, India. Reagents like methanol, acetone, dichloromethane (DCM), potassium hydroxide (KOH), sodium hydroxide (NaOH), and potassium carbonate (K₂CO₃) were purchased from Avra Synthesis Pvt. Ltd., India. All the reagents were used as received. Rice straw was cut into fine pieces of average size in the range of 1–1.5 cm, and stored in zip-lock covers.

Rice straw was characterized by using proximate and ultimate analyses. Proximate analysis was carried out in a thermogravimetric analyzer (TGA) (SDT Q600, T.A. Instruments, Waters GmbH, Austria), as per ASTM E1131-08 [26]. Elemental CHNS composition was obtained by using an elemental analyzer (Thermo Flash 2000, Thermo Fisher Scientific, Austria) according to ASTM D5373-08. Higher heating value (HHV) was determined by using a bomb calorimeter (IKA C2000, I.K.A., Germany) according to ASTM D5865-13. The same analytical methods were adopted to characterize bio-crude and bio-char. The total organic content in the aqueous phase was analyzed by using Karl Fischer Titrator (Metrohm-870 KF Titrino plus, Metrohm AG, Switzerland) according to ASTM D-6304. The proximate analysis, ultimate analysis, and HHV of rice straw are reported in Table 1. These characterization data are in line with the literature [27].

Table 1. Characterization of rice straw.

	Proximate Analysis (wt.%) *				Elemental Analysis (wt.%) **					HHV (MJ kg ⁻¹)
	Volatile Matter	Fixed Carbon	Moisture	Ash	C	H	N	S	O	
Rice Straw	66.1	15.4	5.7	12.8	37.1	5.2	0.5	0.1	44.3	12.1

* Air dried basis; ** dry basis.

2.2. HTL Reactor

HTL experiments were conducted in a custom-built stainless-steel autoclave of 1.3 L volume with 82 mm internal diameter, 25 mm thickness, and 210 mm height. The design temperature and pressure of the reactor were 400 °C and 22 MPa, respectively. The schematic of the reactor setup is provided in Figure 1. An electric coil was wrapped around its surface to provide uniform heat input. The temperature of the reaction mixture was monitored by using a K-type thermocouple, which was connected to a temperature controller. The thermocouple was placed inside the thermo-well, which was fixed to the head of the reactor vessel. A pressure gauge connected to the reactor head was used to monitor the reactor pressure, which was not controlled. Initially, the reaction mixture in the vessel was pressurized by using inert nitrogen gas. The reactor was equipped with an internal cooling coil to quickly bring down the temperature of the reactants. A four-blade turbine impeller was used to thoroughly mix the reactants. The impeller was connected through a zero-leakage magnetic drive with torque capacity of 1.96 N-m. The magnetic drive was cooled by using water circulation when the autoclave reached temperatures higher than 350 °C. The maximum rated speed of the magnetically driven stirrer was 1200 rpm. In order to withstand high pressures, graphite gaskets were used to seal the reactor and its contents. After the reaction, the reactor contents were emptied through a 10 mm diameter opening at the bottom, which was fitted with a flush valve.

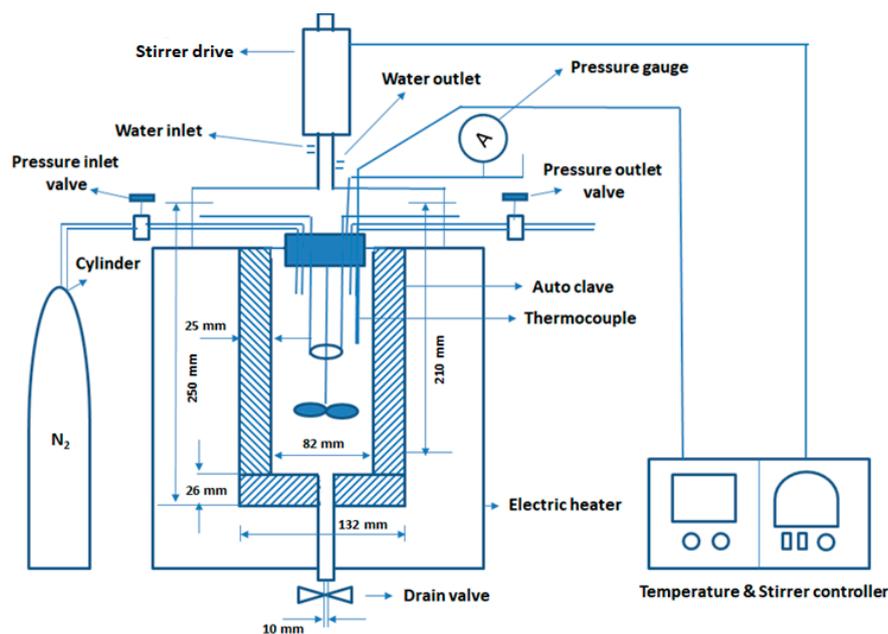


Figure 1. Schematic of the laboratory scale batch HTL reactor.

2.3. Experimental Procedure

In a typical experiment, 30 g of rice straw and 300 mL of solvent were taken in the reactor. The solvent was either water or water:methanol mixtures (75:25, 50:50, and 25:75 vol./vol.%). In order to investigate the effect of water content on bio-crude yield and its composition, rice straw:water composition was also varied as 1:1, 1:5, 1:10, and 1:15 (wt./wt.) in some experiments. In certain experiments, 5 wt.% of alkaline homogeneous catalysts (such as NaOH, KOH, and K_2CO_3) was mixed with water. The autoclave was sealed and then pressurized with nitrogen (N_2) gas. Typically, the initial pressure was 2–6 MPa, which was set based on the final pressure (18 MPa) and temperature (300, 325, and 350 °C) to be reached. The reactants were agitated, using the stirrer at 350 ± 25 rpm. Finally, the reactor was maintained isothermal at the set temperature for 30 and 60 min. After the reaction, the reactor was cooled down to room temperature by continuous circulation of water in the cooling coil and by means of external fan. The gases were released through the release valve, while the liquid product (or bio-crude) was separated from the solid residue (bio-char) by using a solvent-extraction process. The temperature and pressure profiles during the HTL process are depicted in Supplementary Materials Figure S1. It is evident that, in order to reach a final pressure of 18 MPa and 300 °C, the reactor was initially pressurized to ~6 MPa, using N_2 . Within 50–60 min, the operating conditions were attained with a variation of ± 0.5 MPa or ± 5 °C around the set-point value.

The typical procedure for the separation of products is available in Chopra et al. [28]. Briefly, DCM solvent (50 mL) was used to flush the contents of the reactor, which was a viscous kerogen-like mixture containing bio-char, bio-crude, and aqueous-soluble organics. The flushed contents were collected in a beaker and were allowed to settle. The aqueous phase was then separated by decantation in a separation funnel. The DCM-soluble organic fraction was then filtered using a Whatman filter paper (pore size ~ 11 μ m). The bio-char collected on the filter paper was dried at 105 °C and 24 h, and then weighed to calculate its yield. The filtrate was evaporated at 40 °C to obtain the bio-crude. DCM is a better extraction solvent over other common solvents like acetone or hexane, because of its non-polar and volatile nature, and its miscibility with many organic molecules. The use of DCM aids in maximum solubilization of the organics into bio-crude fraction, and easier separation of the aqueous phase from the organic phase. The bio-crude was then weighed to calculate its yield. The autoclave was thoroughly rinsed and washed with both DCM and acetone solvents, to eliminate traces of viscous bio-crude sticking to the reactor wall, cooling coil tubes, and stirrer blades. Most of the HTL

experiments were repeated two times, while some were repeated in triplicate. The standard deviations in product yields are within 2%–5%.

The yields of bio-crude (Y_{BC}), bio-char (Y_{BCh}) and gas+aqueous fractions (Y_{G+AQ}), conversion of rice straw, and energy recovered in bio-crude (ER_{BC}) were calculated by using the following expressions:

$$Y_{BC} (\%) = \left(\frac{M_{BC}}{M_{RS}} \right) \times 100 \quad (1)$$

$$Y_{BCh} (\%) = \left(\frac{M_{BCh}}{M_{RS}} \right) \times 100 \quad (2)$$

$$Y_{G+AQ} (\%) = (100 - Y_{BC} (\%) - Y_{BCh} (\%)) \quad (3)$$

$$\text{Conversion of rice straw} (\%) = \left(\frac{M_{RS} - M_{BCh}}{M_{RS}} \right) \times 100 \quad (4)$$

$$ER_{BC} (\%) = \left(\frac{HHV_{BC} \times M_{BC}}{HHV_{RS} \times M_{RS}} \right) \times 100 \quad (5)$$

In the above expressions, M_{BC} , M_{BCh} , M_{G+AQ} , and M_{RS} denote the mass of bio-crude, mass of bio-char, mass of gas+aqueous fraction, and mass of rice straw, respectively; and HHV_{BC} and HHV_{RS} denote the HHVs of bio-crude and rice straw, respectively.

2.4. Product Characterization

The organic composition of the bio-crude samples was analyzed in a gas chromatograph/mass spectrometer (GC/MS, Shimadzu QP 2020, Shimadzu (Asia Pacific) Pte. Ltd., Singapore). The bio-crude samples were diluted in DCM solvent, and 1 μ L was injected. The GC column, Rxi-5SilMS (30 m length \times 0.25 mm inner diameter \times 0.25 μ m film thickness), was used to separate the compounds. The flow rate of helium gas (99.9995% purity) through the column was 1 mL min^{-1} with split ratio of 1:100. The injector temperature was set at 280 $^{\circ}\text{C}$. The GC column oven temperature was initially maintained at 40 $^{\circ}\text{C}$ for 1 min, followed by a temperature ramp at 5 $^{\circ}\text{C} \text{ min}^{-1}$ to 280 $^{\circ}\text{C}$, and finally held at 280 $^{\circ}\text{C}$ for 5 min. The electron impact ionization voltage was 70 eV, and the ion-source temperature was set at 250 $^{\circ}\text{C}$. The m/z range in the MS was 50–500 Da. Peak identification was done by comparing the mass spectra with NIST14 and Wiley08 mass spectrum libraries, and the identified compounds had a match factor greater than 85%. GC/MS peak area% (or percent selectivity) was used to quantify the various organics in the bio-crude. The organic compounds were classified according to different functional groups.

Non-condensable gases such as CO, CO₂, and H₂ from selected experiments were analyzed in a GC (Agilent 7820A, Agilent Technologies, U.S.A.) equipped with a thermal conductivity detector (TCD). The gas components were separated by using a molecular sieve-13X packed column. The carrier gas was N₂ (99.999% purity), and its flow rate through the column was 3 mL min^{-1} . The gas concentrations were measured by calibrating the column, using standard gas mixtures of different compositions.

3. Results and Discussion

3.1. Effect of Temperature and Reaction Time

Table 2 presents the mass conversion of rice straw and the yields of bio-crude, bio-char, and gas+aqueous fractions at different temperatures (300, 325, and 350 $^{\circ}\text{C}$) and residence time periods (30 and 60 min), using water as the solvent. The mass conversion of biomass exhibits reasonable trends with the operating conditions. At any reaction time, the conversion increases with increasing temperature, as a result of the greater hydrolytic decomposition of rice straw at high temperatures. Increasing the reaction time leads to only a marginal increase in conversion of the feedstock to bio-crude and gas+aqueous fraction, which is evident by comparing the results of R1–R3 versus R4–R6. However,

reaction time plays a major role in the distribution of bio-crude and gas+aqueous fractions. At 300 °C, increasing the reaction time enhances the yield of bio-crude, while at 350 °C, significant enhancement in the yield of gas+aqueous fraction is evidenced. It is also important to note that, owing to a high amount of ash in rice straw, which adds to its recalcitrance, obtaining conversions more than 80 wt.% may not be possible.

Table 2. Effect of final temperature and reaction time on conversion of rice straw and product yields, using water as solvent at rice-straw-to-water ratio of 1:10.

Expt. Code	Temperature (°C)	Reaction Time (min)	Conversion (%)	Bio-Crude Yield (wt.%)	Bio-Char Yield (wt.%)	Gas + Aqueous Yield (wt.%)
R1	300	30	75.5	10.8 ± 0.4	24.6 ± 0.5	64.6
R2	325	30	74.4	15.1 ± 0.6	25.6 ± 1.3	59.3
R3	350	30	78.6	12.9 ± 0.7	21.4 ± 0.8	65.7
R4	300	60	75.2	12.3 ± 1.5	24.8 ± 1.8	62.9
R5	325	60	77.1	9.2 ± 0.5	22.9 ± 0.7	67.9
R6	350	60	80.0	3.1 ± 1.2	20.0 ± 0.3	76.9

The effect of temperature on bio-crude yield is evident from Table 2 at similar processing times. For example, after 30 min of processing time, the bio-crude yields followed the trend 15.1 wt.% (325 °C) > 12.9 wt.% (350 °C) > 10.8 wt.% (300 °C). Increasing the temperature from 300 to 350 °C at 60 min processing time led to a significant decrease in the yield of bio-crude (12.3 to 3.1 wt.%), with a concomitant increase in gas+aqueous yield (62.9 to 76.9 wt.%) and only a minor drop in bio-char yield. This suggests that thermal decomposition and degradation of the organic components are predominant at high temperatures. However, at a lower temperature of 300 °C, increasing the reaction time to 60 from 30 min leads to an enhancement in bio-crude yield, without significant change in conversion. This shows that temperature and processing time do have a combined effect on bio-crude yields. At 30 min processing time, a maximum bio-crude yield of 15.1 wt.% was achieved at 325 °C, while at 60 min, a maximum bio-crude yield was obtained at 300 °C. Run-dong et al. [29] studied HTL of rice stalks at various reaction time periods (30–120 min) and temperatures (250–375 °C), in the presence of ethanol. At 250 °C, a maximum bio-crude yield of 48 wt.% was obtained at an optimal reaction time of 90 min, whereas the highest bio-crude yield, of 55 wt.%, was obtained at 60 min and 325 °C. This shows that, at a high temperature, a shorter residence time may be sufficient to achieve high bio-crude yield. However, the optimum operating condition is not only determined by bio-crude yield, but also by other bio-crude quality markers, such as HHV, and elemental composition (H/C and O/C).

Table 3 depicts the elemental composition and HHV of bio-crude and bio-chars obtained from experiments R1–R6. The HHVs of bio-crude were calculated by using the correlation developed by Francis and Lloyd [30]: $\text{HHV (MJ kg}^{-1}\text{)} = (34 [\%C] + 124.3 [\%H] + 6.3 [\%N] + 19.3 [\%S] - 9.8 [\%O])/100$. As explained earlier, 350 °C–60 min corresponds to a severe condition that leads to low carbon content in bio-crude, in addition to low yield. As a result, the HHV of bio-crude is also the lowest as compared to other experiments performed in this study. It is important to note that the quality of bio-crude is better from experiment R4, corresponding to 300 °C–60 min. This is evident from the high carbon (77.6 wt.%) and low oxygen content (15.3 wt.%). The HHV of the bio-crude obtained at this condition is also high (35 MJ kg⁻¹), and it is in accordance with the oxygen content. In order to further ascertain which operating condition is the optimum, the energy recovery in bio-crude was assessed. Energy recovery in bio-crude depends on both bio-crude yield and its HHV, according to Equation (5). At 300 °C–60 min, the energy recovery of ~36% is due to both high HHV of bio-crude (35.3 MJ kg⁻¹) and its reasonable yield (12.3 wt.%). Moreover, the hydrogen content in bio-crude is maximum (8.4 wt.%) at this condition, and the atomic H/C and O/C ratios are 1.31 and 0.14, respectively. The HHVs of bio-crudes observed in this study are in line with that reported in the HTU[®] (Hydrothermal Upgradation) process of Shell Research Laboratory for a variety of biomass feedstocks [7]. A preliminary analysis of the non-condensable gases produced at this condition was performed, using GC–TCD. The major gases

were CO₂ (74 vol.%), CO (18 vol.%), CH₄ (6 vol.%), and H₂ (2 vol.%) on N₂-free basis. The high amount of CO₂ generated can be attributed to the decarboxylation reactions, which are dominant than the CO removal through decarbonylation during HTL. When compared to fast pyrolysis bio-oil from rice straw, which contains 42%–49% of oxygen [31,32], HTL bio-crude from rice straw at the optimal processing condition contains three times lower oxygen (14.2%), which demonstrates its superior quality. Therefore, further experiments involving different rice straw:water ratios, and water:methanol ratios were performed at a final temperature of 300 °C and 60 min residence time.

Table 3. Effect of final temperature and reaction time on elemental composition of bio-crude and bio-char, HHV of bio-crude and bio-char, and energy recovered in bio-crude. The rice-straw-to-water ratio is 1:10 wt./wt.

Expt. Code	Temp. (°C)	Time (min)	Elemental Composition of Bio-Crude (wt.% db)				HHV of Bio-Crude (MJ kg ⁻¹)	Elemental Composition of Bio-Char (wt.% db)				HHV of Bio-Char (MJ kg ⁻¹)	ER _{BC} (%)
			C	H	N	O*		C	H	N	O#		
R1	300	30	72.9	7.9	0.3	18.9	32.7	51.6	4.5	0.4	30.7	20.1	29.4
R2	325	30	73.5	7.0	0.5	19.0	31.9	46.6	3.4	0.3	36.9	16.5	39.8
R3	350	30	69.2	6.9	0.6	23.2	29.8	53.4	3.8	0.4	29.6	20.0	31.7
R4	300	60	77.1	8.4	0.4	14.1	35.3	51.3	4.3	0.2	31.4	19.8	35.9
R5	325	60	73.3	7.0	0.4	19.3	31.7	39.5	3.2	0.3	44.2	13.1	24.1
R6	350	60	65.7	6.4	0.5	27.4	27.6	49.7	3.4	0.4	33.7	17.8	7.1

* %O = 100-(%C + %H + %N), # %O = 100-(%C + %H + %N + %Ash). db: dry basis. ER: energy recovered in bio-crude (%).

The elemental composition of bio-char from various experiments is depicted in Table 3. It is clear that most of the oxygen present in the feedstock is transferred to the bio-char in HTL experiments. This is reflected in the high oxygen content (28–44 wt.%) in bio-char. The carbon content in bio-chars is lower than that present in bio-crude, but certainly better than rice straw feedstock. As a result, the HHVs of majority of bio-chars are higher (17–21 MJ kg⁻¹) than that of the rice straw (12.1 MJ kg⁻¹). The production of bio-char can be attributed to both fixed carbon present in the feedstock and the repolymerization reactions occurring at long residence periods during the process. The repolymerization reactions are particularly important at high pressures and low temperatures. At higher temperatures, there is a possibility of the oxygenates and hydrocarbons to get converted to non-condensable gases.

3.2. Effect of Rice-Straw-to-Water Ratio

Figure 2 depicts the product yields when the mass ratio of rice straw to water is varied at the optimal condition of 300 °C–60 min. It is evident that the bio-crude yield increases from 5.7 to 12.3 wt.% when the rice-straw-to-water ratio is increased from 1:1 to 1:10 wt./wt. The further increase in water content decreases the bio-crude yield to 5.8 wt.%. Generally, a high amount of the solvent leads to better extraction of the organics produced during the HTL process by the denser solvent medium [33]. This is supported by the trend followed by bio-char yield: 35.5 wt.% (1:1 wt./wt.) > 25 wt.% (1:5 wt./wt.) ≈ 24.8 wt.% (1:10 wt./wt.) > 23.9 wt.% (1:15 wt./wt.). However, rice-straw-to-water ratio of 1:10 wt./wt. is found to be the optimal condition for maximum bio-crude production. The HHV of bio-crude increased from 33.9 to 35.3 MJ kg⁻¹ with the increase in rice-straw-to-water ratio from 1:1 to 1:10 wt./wt., and then decreased to 33.7 MJ kg⁻¹ with further increase, up to 1:15 wt./wt. This is attributed to the increase of oxygen content in bio-crude to 15.3 from 14.1 wt.% as the water content was increased. Maximum gas+aqueous yield of 70 wt.% was obtained with 1:15 wt./wt. of rice straw: water, which shows that small-molecule oxygenates of the bio-crude were probably converted to gases. Moreover, it is possible that high water content in the feedstock can solvate the small molecule oxygenates, and so they get transferred to the aqueous phase. Therefore, 1:10 wt./wt. is verified to be the optimal rice straw:water composition.

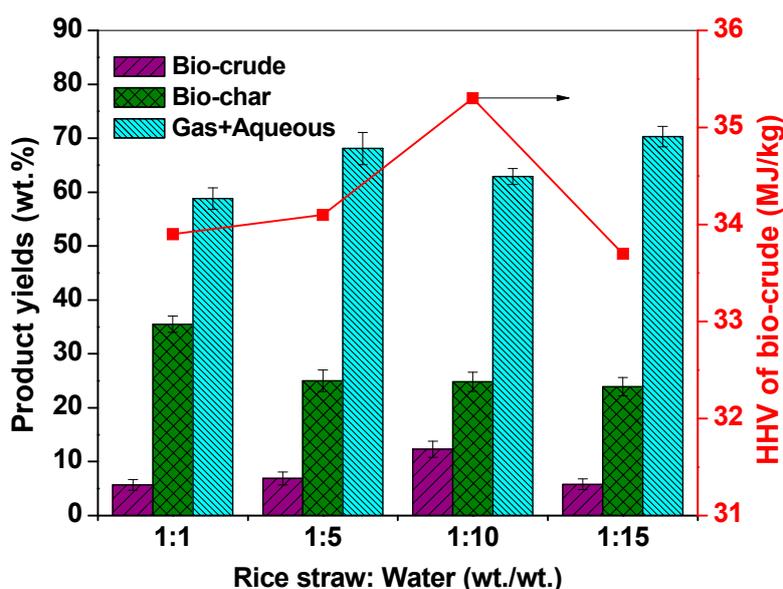


Figure 2. Effect of rice-straw-to-water ratio on product yields and HHV of bio-crude at a final temperature of 300 °C and 60 min.

3.3. Influence of Methanol as a Co-Solvent

Co-solvents play a significant role in enhancing the production of bio-crude because of the strong and specific interactions with biomass intermediates. Co-solvents are found to be more effective than an individual solvent for bio-crude production from biomass via HTL [9]. In fact, the effect is due to both physical and chemical factors. The critical point of methanol (239 °C, 8.09 MPa) is low as compared to that of water (374 °C, 22.1 MPa). The critical temperature and pressure values of various methanol:water mixtures (in vol.%/vol.%) were calculated by using ASPEN plus V8.6 software, and they followed the trend 25:75 (352.7 °C, 19.9 MPa) > 50:50 (325.5 °C, 17 MPa) > 75:25 (289.5 °C, 13.3 MPa). The dielectric constant of methanol is low as compared to that of water. Therefore, methanol can readily dissolve the high molecular weight organics generated from rice straw decomposition. Moreover, at 50:50 and 75:25 compositions of methanol:water, supercritical condition prevails at the operating condition. Therefore, these are expected to significantly affect the product yields and their composition. The chemical effect of methanol is its ability to donate hydrogen. Pedersen et al. [34] reported that radicals formed from hydrogen-donating solvents can act as radical quenching mediators and prevent the lignin-derived radicals from participating in repolymerization reactions. Other studies have reported that alcohols help to dissolve and stabilize the intermediates. This reduces their rate of repolymerization, which eventually enhances the bio-crude yield [35,36]. The hydrogen donor solvents enhance the hydrogenolysis reactions of biomass. In their absence, the formed radicals from rice straw can recombine to form high-molecular-weight compounds, which eventually increase the yield of bio-char.

Figure 3 depicts the yields of product fractions and the HHVs of bio-crudes obtained at different water:methanol compositions. Clearly, the presence of methanol as co-solvent improves the yield of bio-crude, which follows the trend 31.7 wt.% (50:50 water:methanol) > 16.4 wt.% (25:75) > 14.4 wt.% (75:25) > 12.3 wt.% (100:0). The bio-char yield follows a clear trend with water:methanol composition, as follows: 20.76 wt.% (25:75) > 18.5 wt.% (50:50) > 14.9 wt.% (75:25).

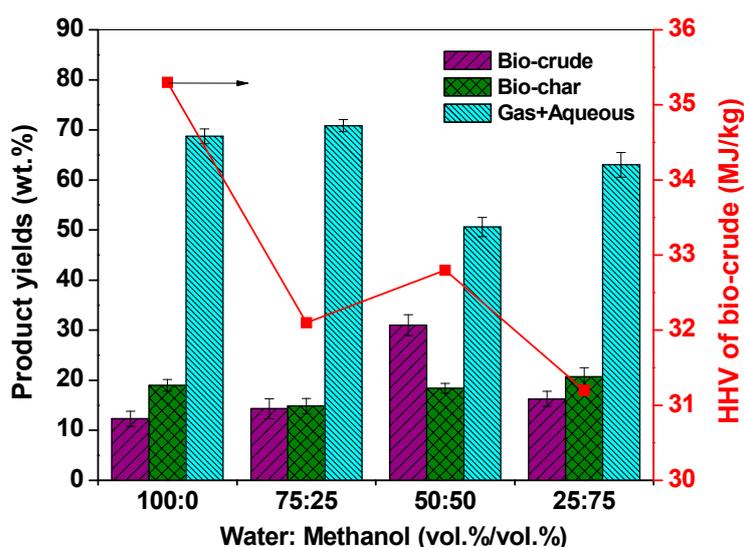


Figure 3. Effect of water-to-methanol ratio on product yields and HHV of bio-crude at a final temperature of 300 °C, 60 min reaction time, and rice-straw-to-solvent ratio of 1:10 wt./wt.

In order to ascertain the quality of bio-crudes obtained by using methanol as co-solvent, the elemental composition and HHVs were analyzed. From Table 4, it is clear that the oxygen content in bio-crude is, in fact, higher (17.8–22.3 wt.%) as compared to that obtained with only water as the solvent. The carbon content in bio-crude is lower (69–72 wt.%) as compared to that when methanol was not used. With equal composition mixture of water:methanol (experiment R11), the oxygen content is reasonably low (17.8 wt.%), which leads to better HHV of bio-crude at this condition. Contrary to the expectation, there is no significant improvement in hydrogen content of the bio-crude, while oxygen is improved. This indicates the participation of methanol in reactions with the hydrolysis intermediates from biomass during HTL. This is evident in the formation of high amounts of oxygenated compounds, like esters in bio-crude, which is discussed in Section 3.5. The HHVs of bio-crudes are in line with the oxygen content in them. The HHV recorded with 50:50 (vol.%/vol.%) water:methanol was 32.8 MJ kg⁻¹. Li et al. [37] conducted HTL of sludge in supercritical ethanol and showed that oxygen content in bio-crude passed through a maxima as ethanol:water content was varied. They attributed this to the competition between hydrogen donor reduction of oxygen, and CO–CO₂ reduction of oxygen. In this study, oxygen content is minimum with equal composition mixture of methanol:water, which then increases with the addition of methanol. This shows that more methanol in the mixture possibly leads to hydrogen donor reduction of oxygen, which leads to dehydration. Thus, a lower amount of oxygen from biomass is lost as water, as compared to a higher amount of oxygen loss in the form of CO₂ and CO.

The bio-char obtained from experiments conducted with methanol (R10–R12) contained a high amount of oxygen and low amount of carbon in them. This is reflected in their poor HHVs (<15.7 MJ kg⁻¹). This shows that, besides getting converted to oxygenates in bio-crude, a significant fraction of methanol is involved in the formation of bio-char. This occurs by the formation of high-molecular-weight oxygenated polymerized fragments. The analysis of non-condensable gases collected at the end of the HTL process conducted with equal composition of water:methanol (experiment R11) showed 40 vol.% of CO₂, 46.7 vol.% of CO, and 13.3 vol.% of H₂. As compared to experiment R4 conducted with only water as solvent, the CO₂ production is significantly low in this experiment. Methanol decomposition is reported to occur via two pathways. In one pathway, methanol reacts with water under HTL conditions, to form CO₂ and H₂. In another pathway, methanol initially decomposes, to form formaldehyde and H₂. Formaldehyde further decomposes to CO and H₂ [38]. Finally, CO can get converted to CO₂ by reacting with water. The observed gas composition demonstrates that the second pathway is favored when methanol is added as a co-solvent.

Table 4. Effect of water-to-methanol ratio and catalysts on elemental composition of bio-crude and bio-char, and HHVs of bio-crude and bio-char at final process temperature of 300 °C, reaction time of 60 min, and rice-straw-to-solvent ratio of 1:10 wt./wt.

Expt. Code	Water: Methanol (Vol.%/Vol.%)	Elemental Composition of Bio-Crude (wt.% db)				HHV of Bio-Crude (MJ kg ⁻¹)	Elemental Composition of Bio-Char (wt.% db)				HHV of Bio-Char (MJ kg ⁻¹)
		C	H	N	O*		C	H	N	O#	
R10	75:25	71.5	7.7	1.6	19.2	32.1	44.4	3.4	1.7	37.7	15.7
R11	50:50	72.7	7.8	1.7	17.8	32.8	36.4	3.1	1.3	46.4	11.7
R12	25:75	69.1	7.7	2.3	20.9	31.2	30.8	2.7	1.1	52.6	8.7
R13	50:50 ⁽¹⁾	71.7	7.7	2.3	18.3	32.3	27.4	2.7	1.0	56.1	7.2
R14	50:50 ⁽²⁾	73.5	7.9	2.4	16.2	33.3	23.4	2.3	0.8	60.7	4.8
R15	50:50 ⁽³⁾	73.8	7.7	2.3	16.2	33.2	23.3	2.3	0.8	60.8	4.9

*%O = 100-(%C + %H + %N), #%O = 100-(%C + %H + %N + %Ash), ⁽¹⁾ KOH (5 wt.%), ⁽²⁾ NaOH (5 wt.%), and ⁽³⁾ K₂CO₃ (5 wt.%) were employed as catalysts. In R10, R11, and R12, no catalyst was used.

3.4. Role of Alkali Catalysts

The addition of homogeneous catalysts, such as alkali salts, is known to improve the bio-crude yield in the HTL process, owing to the inhibition of dehydration reaction of the carbohydrate fraction of the biomass [7]. This is particularly evident at high pH values of the mixtures upon the addition of alkali. Moreover, hydrothermal gasification and water–gas shift reactions are promoted by the alkali catalysts [7]. Alkali catalysts such as KOH, K₂CO₃, Na₂CO₃, and NaOH have been tested for HTL of agro residues, forest wastes, and municipal solid waste mixtures [39,40]. In this study, 5 wt.% of KOH, K₂CO₃, and NaOH was used as catalysts for HTL of rice straw at 300 °C–60 min, rice-straw-to-solvent ratio of 1:10 (wt./wt.), and water-to-methanol ratio of 50:50 (vol./vol.). Figure 4 depicts the product yields and the HHVs of bio-crudes. It is evident that the use of alkali catalysts significantly improved the bio-crude yield, which follows the trend KOH (39.9 wt.%) > NaOH (34.5 wt.%) > K₂CO₃ (33.8 wt.%) > no catalyst (31.7 wt.%). Among the three catalysts, K₂CO₃ was most effective for overall mass conversion of rice straw to bio-crude and gas+aqueous fractions. The maximum conversion of 86.9% was obtained with K₂CO₃, followed by 84.6% for NaOH, 83.5% for KOH, and 81.6% without any catalyst.

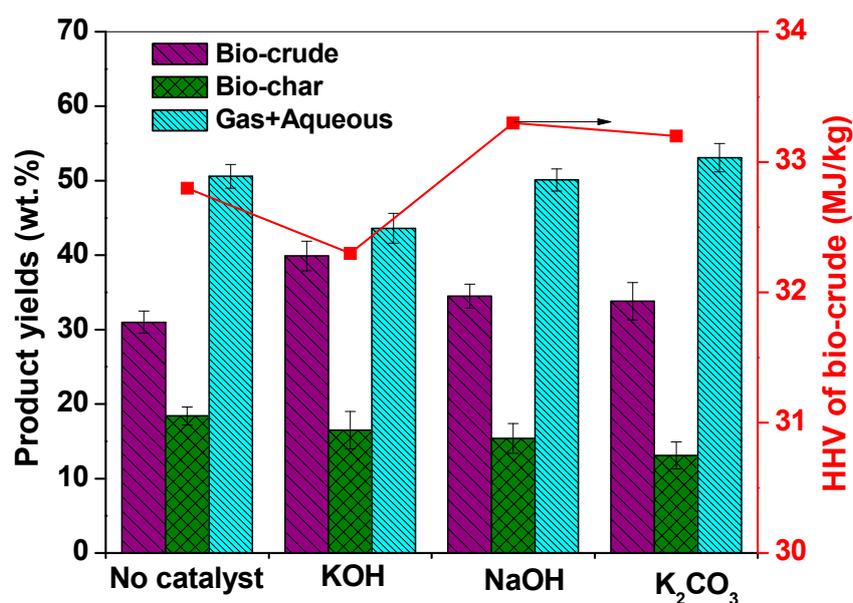
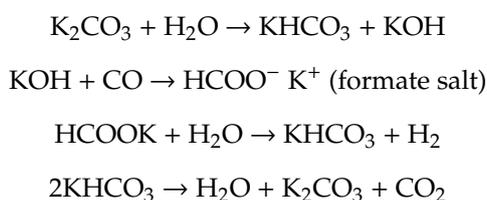


Figure 4. Effect of alkali catalysts on product yields and HHV of bio-crude at 300 °C, 60 min, rice straw:solvent ratio of 1:10 wt./wt., catalyst quantity of 5 wt.%, and 50:50 (vol./vol.%) methanol:water.

Generally, carbonates are shown to be effective as catalysts for the HTL process, compared to hydroxides. The mechanism of action of K_2CO_3 is proposed to follow the reaction sequence given by [7]:



The high yield of gas+aqueous (53.1 wt.%) produced using K_2CO_3 substantiates its effectiveness in improving the conversion of rice straw via hydrolytic decomposition of carbohydrates and lignin components. The reported gas+aqueous yields are in line with the value reported by Zhu et al. [41]. Even though the bio-crude yield was high with KOH, the oxygen content is lower (16 wt.%) and carbon content is higher (73–74 wt.%) in bio-crudes produced using NaOH and K_2CO_3 . As a result, the HHVs of bio-crudes are slightly better (33 MJ kg^{-1}) with NaOH and K_2CO_3 catalysts as compared to that from KOH (32 MJ g^{-1}). The molar H/C and O/C content in bio-crudes vary in the range of 1.25–1.30 and 0.17–0.19, respectively. From the elemental composition of bio-char, it is clear that the use of these alkali salts, along with methanol co-solvent, significantly improves the oxygen retained in the bio-char. The high oxygen (56–60 wt.%) and low carbon (23–27 wt.%) lead to low HHVs of bio-chars. Table 5 presents a comparison of bio-crude yields and their salient properties from rice straw, using different solvent systems. It is evident that the yield of bio-crude obtained using methanol as co-solvent is comparable with that using 2-propanol. Importantly, the HHV of bio-crude is better and oxygen content in it is lower with the methanol–water system as compared to 2-propanol–water and ethanol–water systems. This substantiates the positive effect of methanol as a co-solvent for HTL of rice straw.

Table 5. Comparison of bio-crude yield and its properties reported in the literature with this study.

Temp. (°C)	Rice Straw (g)	Solvent (mL)	Solvent: Water (Vol./Vol.)	Solvent	Bio-Crude Yield (wt.%)	HHV (MJ kg ⁻¹)	O (wt.%)	C (wt.%)	Ref.
300	20	300	-	Water	29.1	27.2	45.3	47.4	Yuan et al. [18]
	20	300	-	Ethanol	13.0	33.5	-	-	
	20	300	1:1	Ethanol–water	38.4	29.7	-	-	
	20	300	-	2-Propanol	15.1	35.8	18.5	71.3	
	20	300	1:1	2-Propanol–water	39.7	30.7	27.3	63.8	
300	30	300	-	Water	12.3	35.3	14.1	77.1	This study
	30	300	1:1	Methanol–water	36.8	32.8	17.8	72.7	
	30	300	1:1	Methanol–water+KOH	40.0	32.3	18.3	71.7	

3.5. Bio-Crude Composition

Bio-crudes from selected experiments were analyzed, using GC/MS, to analyze the variation of organic composition with respect to the process parameters. The various organic compounds present in the bio-crude were classified according to the functional groups, namely simple oxygenates, cyclo-oxygenates, aliphatic hydrocarbons, phenolics, other aromatics, indene derivatives, furan derivatives, and esters. The category of other compounds includes N-containing organics and those that were obtained with low match factor in GC/MS. Simple oxygenates were mostly linear-chain-substituted ketones, while cyclo-oxygenates contained mostly cyclopentenone and alkyl-substituted cyclopentenones. Aromatics included primarily non-phenolic compounds like aromatic hydrocarbons and aromatic oxygenates. Figure 5 depicts the selectivities to functional groups when 1:10 wt./wt. of rice straw:water was used at various conditions. The major product groups were found to be cyclo-oxygenates, phenolics, and other aromatics. It is evident that, with the increase in residence time of the process, from 30 to 60 min, the selectivity to phenolic compounds decreased slightly. The marginal decrease in selectivity to phenolics from 53.7% (30 min) to 50.4% (60 min) at

300 °C, and 49.9% (30 min) to 49.3% (60 min) at 325 °C can be attributed to simultaneous formation of phenolic compounds from the lignin fraction at longer processing time and the decomposition of phenols to aromatic hydrocarbons via dehydration and demethoxylation pathways. Moreover, a major reduction in selectivity to cyclo-oxygenates accompanied by an increase in the formation of non-phenolic aromatic compounds were observed. In fact, the combined selectivity to non-phenolic aromatics and indene derivatives increased significantly as the processing time was increased. For example, at 300 °C, it increased from 6.6% to 21.2%, while at 325 °C, it increased from 6.6% to 18.8%.

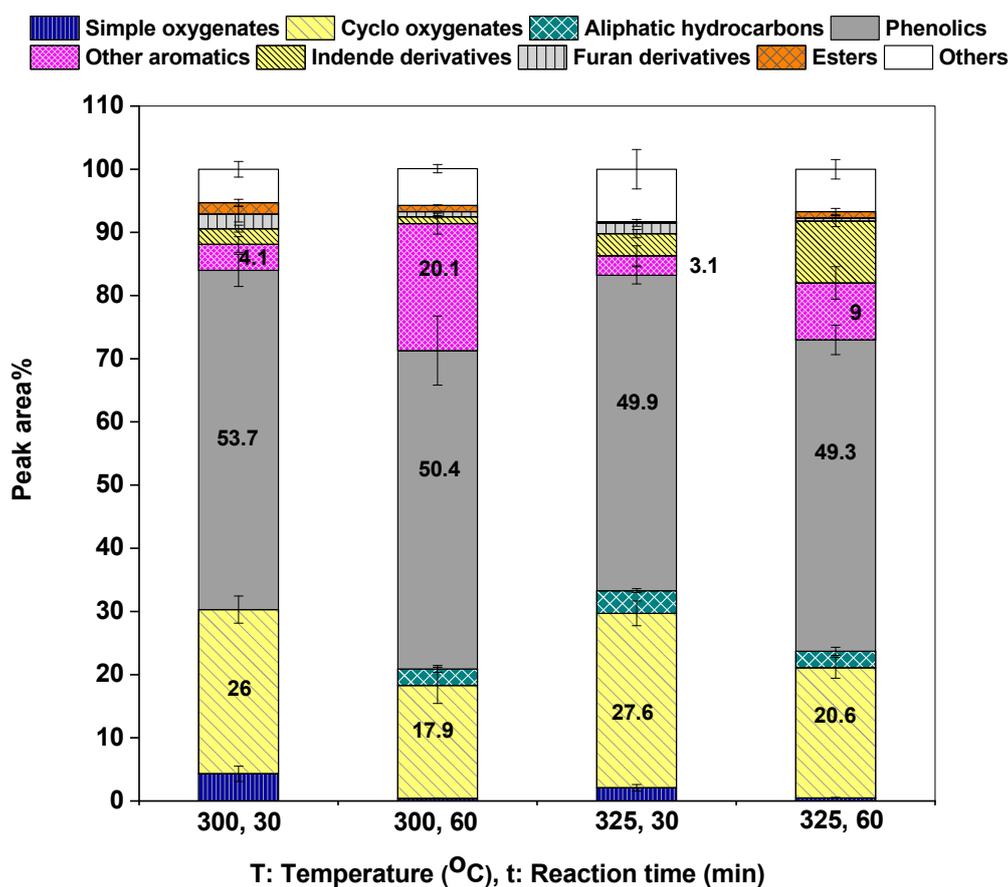


Figure 5. Selectivity to various functional groups in bio-crude obtained at rice-straw-to-water ratio of 1:10 wt./wt., at different operating conditions.

The major phenolic compounds in the bio-crude were phenol, 2-methylphenol (o-cresol), 4-ethylphenol, catechol, guaiacol, 4-ethylguaiacol, alkyl-substituted benzenediols, hydroxyl acetophenone, and syringol. Phenolic compounds are derived from the decomposition of lignin, mainly via hydrolytic cleavage of α -O-4 and β -O-4 linkages [42]. Pelzer et al. [43] proposed a mechanism of acidolysis of lignin model compounds, which involved nucleophilic attack of water on α -carbon that led to α -O-4 aryl-ether bond cleavage. This mechanism was commensurate with the protonation of ether oxygen. Similar reactions in the HTL process are responsible for the formation of observed products.

An increase in processing time clearly decreases the selectivity to cyclo-oxygenates, which can be attributed to their decomposition to form non-condensable gases, like CO and CO₂, in addition to other low molecular oxygenates, which were not detected in the gas phase in this study. For example, at 300 °C, the decrease was from 26% (30 min) to 17.9% (60 min), while it was 27.6% (30 min) to 20.6% (60 min) at 325 °C. The major cyclo-oxygenates were cyclopentanone, 2-cyclopentene-1-one, 3-methyl-2-cyclopentene-1-one, 2,3-dimethyl-2-cyclopentene-1-one, 2,3,4-trimethyl-2-cyclopentene-1-one, and 2-acetyl-cyclopentanone. The cyclopentanones are mainly produced by the decomposition of the pentanose sugars present in the hemicellulose

fraction of biomass. A few cyclohexanone derivatives were also observed in the bio-crude, and their formation can be traced to the successive hydrolytic dehydration of hexose sugars from the cellulose fraction. Interestingly, the decrease in production of cyclo-oxygenates at 60 min is accompanied by an increase in production of aromatic compounds such as methoxy-substituted benzenes, naphthalenol, naphthol, hydroxy-substituted naphthalene derivatives, and methyl- and hydroxy-substituted indanone. This indicates that, at long residence times, bimolecular condensation reactions of cyclo-oxygenates with low-molecular-weight compounds are prevalent during HTL.

The temperature effect is not significant for the production of these compounds in the bio-crude at similar processing periods. For example, at 60 min, the selectivities to phenolic compounds are comparable (50.4% at 300 °C vs. 49.3% at 325 °C), while the selectivities of total aromatics (combined non-phenolic aromatics and indene derivatives) are only slightly different (21.2% at 300 °C vs. 18.8% at 325 °C). Similarly, at 30 min, the selectivities to cyclo-oxygenates (26% vs. 27.6%) and total aromatics (6.6% at 300 and 325 °C) are very much comparable. Therefore, the effect of increase in temperature, at least in the range investigated in this study, is minimal on composition of major functional groups in bio-crude. Figure 6 depicts the structures of the salient products produced from HTL of rice straw in presence of water as the solvent. Supplementary Tables S1–S4 provide the list of classified organic compounds detected in the bio-crude at different conditions, along with their composition. A number of compounds identified in this study are in agreement with Liu et al. [44], who carried out HTL of walnut shells in the presence and absence of alkali.

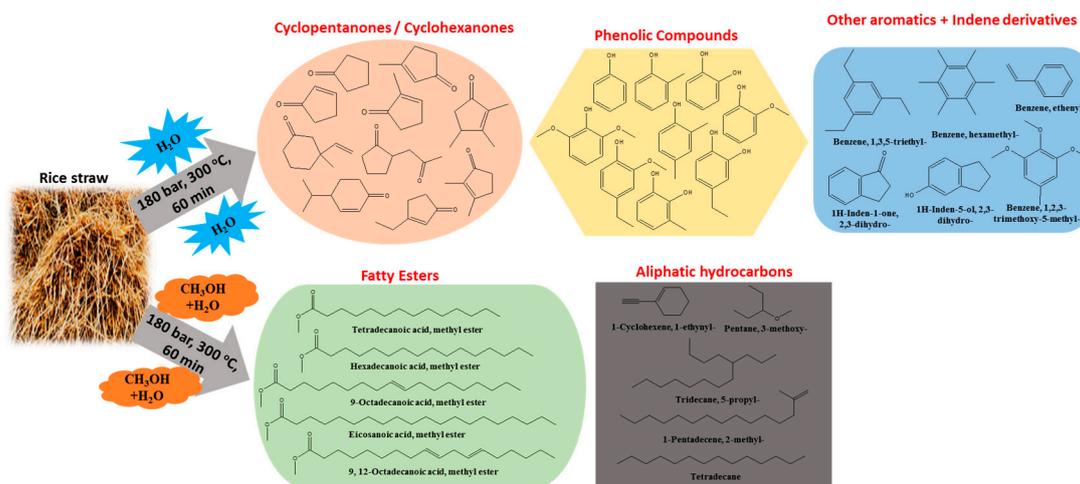


Figure 6. Scheme depicting the typical products produced from HTL of rice straw at different conditions.

The effect of water:methanol and alkali catalysts on bio-crude composition is shown in Figure 7a. The detailed lists of classified organics under each product group at different water:methanol volume ratios are available in Supplementary Tables S5–S7. It is evident that the addition of methanol to water significantly alters the organic distribution in the bio-crude. Esters, mostly methyl esters, emerge as the major organic compounds. Compared to the case with only water as the solvent, the addition of methanol enhances the production of methyl esters, possibly via esterification/methanolysis reactions of the carboxylic functional groups present in the biomass intermediates, which is similar to reported results [10,45]. The subcritical/supercritical medium of methanol–water can catalyze these reactions, owing to the strong acidic–basic nature. The selectivity to esters in the bio-crude follows the trend 72.9% (25:75 vol./vol.% water:methanol) > 59.6% (75:25) > 51.5% (50:50). Interestingly, a similar trend is followed by the oxygen content in the respective bio-crudes (Table 4). This validates the high HHV of bio-crude when an equal composition mixture of water:methanol is used as the solvent system (Figure 3). The major esters include octadecanoic acid–methyl ester, hexadecanoic acid–methyl ester, and tetradecanoic acid–methyl ester. Generally, the high selectivity to esters is accompanied by lower selectivities to cyclo-oxygenates and phenolic compounds. More importantly, it is worthwhile

to mention that with 25:75 water:methanol mixture, the operating condition of 300 °C–18 MPa is supercritical, while for 75:25 and 50:50 water:methanol mixtures, the operating condition is still subcritical and near critical, respectively. This can lead to significant differences in solubility of the components in bio-crude, which has resulted in the observed distribution. The production of simple/linear oxygenates, aliphatic hydrocarbons, furan derivatives, and indene derivatives was negligible in the bio-crude when methanol was added as a co-solvent. Li et al. [37] observed ethyl esters and butyl esters of long-chain carboxylic acids (C15–C20) and fatty acids (mainly octadecanoic acid) as the major components in the bio-crude from sludge in the presence of supercritical ethanol. This supports the organic distribution in bio-crude observed in this study. Figure 6 depicts the structures of the salient esters and aromatic compounds produced from rice straw when methanol was used as the co-solvent.

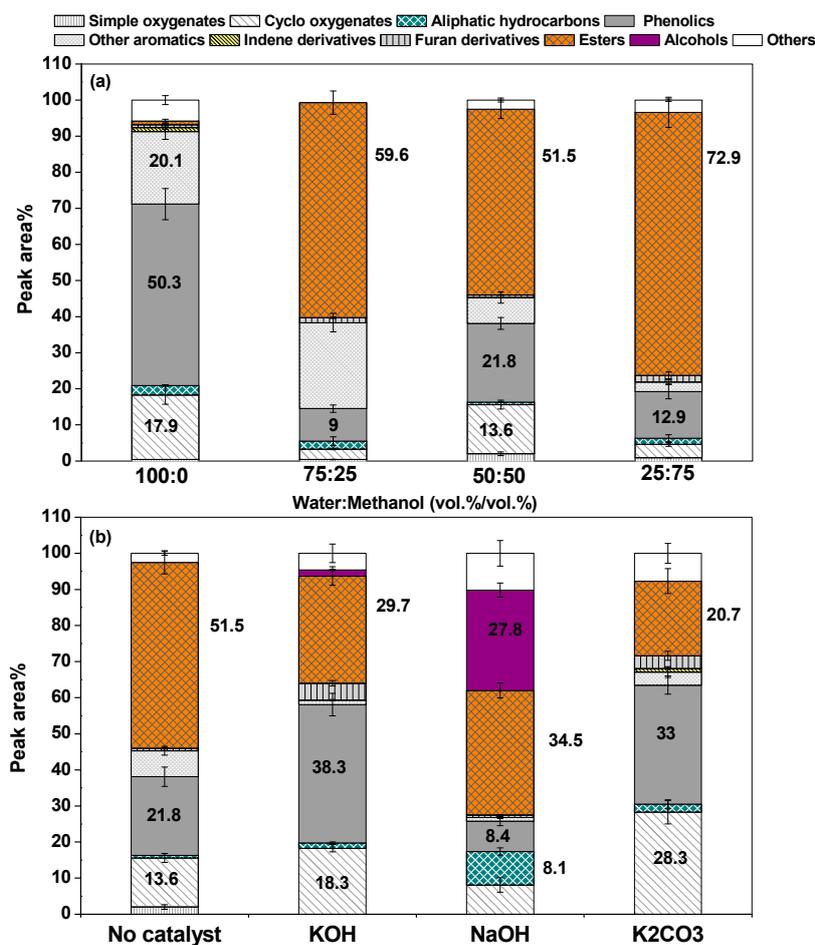


Figure 7. Selectivity to various functional groups in bio-crude obtained at (a) different water-to-methanol ratios and (b) different alkali catalysts at water:methanol of 50:50 (vol.%/vol.%). The final temperature is 300 °C, reaction time is 60 min, and rice-straw-to-solvent ratio is 1:10 wt./wt.

Figure 7b depicts the organic distribution in bio-crude from rice straw when the alkali catalysts were used in the presence of an equal composition mixture of methanol:water. The detailed lists of products in the bio-crude classified according to functional groups are available in Supplementary Tables S8–S10. It is evident that the selectivity to esters is greatly reduced upon the addition of the alkali catalysts, which shows that these promote hydrolysis reactions over esterification, which is due to the effect of methanol in the reaction mixture. The selectivities to esters follow the trend: no catalyst (51.5%) > NaOH (34.5%) > KOH (29.7%) > K₂CO₃ (20.7%). Significant production of phenolic compounds is observed in the presence of KOH (38.3%), followed by K₂CO₃ (33%) and un-catalyzed system

(21.8%). The addition of NaOH, interestingly, favors the production of alcohols, mainly dodecanol and tetradecanol, which shows that hydroxylation is favored in presence of NaOH. The production of long-chain hydrocarbons is also favored (~8% selectivity in presence of NaOH), but the phenolics were greatly suppressed. For HTL of woody biomass, it is reported that potassium salts exhibit better catalytic activity as compared to sodium salts, which follow the trend $K_2CO_3 > KOH > Na_2CO_3 > NaOH$ [7]. Importantly, the role of alkali salt depends on the biomass type to a certain extent, and the solvent medium to a great extent. Therefore, the observed variations in product distribution are specific to the reaction mixture considered in this study. Between KOH and K_2CO_3 , the former is found to be effective for the hydrolytic cleavage of lignin to produce phenolics, while the latter exhibits relatively better activity for hemicellulose hydrolysis to produce more of cyclo-oxygenates.

3.6. Process Energy Balance

In order to evaluate the energy consumed by various streams and the process as a whole, a detailed energy balance of the process for experiments R4, R11, and R13 was performed. These experiments were performed at a final temperature of 300 °C and residence time of 60 min. The percent energy recovery and energy-consumption ratio were determined according to the following expressions [46,47]:

$$\text{Energy recovery (ER) (\%)} = \frac{E_P}{E_F + Q_S} \times 100 \quad (6)$$

$$\text{Energy consumption ratio (ECR)} = \frac{E_{HTL}}{E_{BC}} \quad (7)$$

where E_P , E_F , E_{HTL} , E_{BC} , and Q_S denote the total energy of products, energy of the feedstock, heat required for the HTL process, energy recovered in bio-crude, and heat of solvent, respectively. These terms are defined as follows [46,47]:

$$E_P = (M_{BC} \times HHV_{BC}) + (M_{BCh} \times HHV_{BCh}) + (M_G \times HHV_G) \quad (8)$$

$$E_F = (M_{RS} \times HHV_{RS}) \quad (9)$$

$$E_{HTL} = \frac{(Q_S + Q_{RS}) \times (1 - \eta_h)}{\eta_c} \quad (10)$$

$$E_{HTL} = \frac{((m_S \times C_{p,S} \times \Delta T) + (m_{RS} \times C_{p,RS} \times \Delta T)) \times (1 - \eta_h)}{\eta_c} \quad (11)$$

$$E_{BC} = (M_{BC} \times HHV_{BC}) \quad (12)$$

In the above expressions, m_S , m_{RS} , $C_{p,S}$, $C_{p,RS}$, and ΔT denote the mass of solvent, mass of rice straw, specific heat capacity of solvent, specific heat capacity of rice straw, and temperature difference, respectively. Q_{RS} and Q_S denote the heat required to raise the temperature of rice straw and solvent, respectively. When water–methanol mixtures were used as solvents, Q_S was calculated by mixture rule. The factors η_h and η_c in Equation (11) denote the efficiencies of heat recovery and combustion energy, respectively, and correspond to the scenario of bio-crude combustion. The values of these are modestly assumed as 0.5 and 0.7, respectively [47]. The sample calculations are provided in Supplementary S11.

Table 6 depicts the energy values for three experiments. It is evident that the energy recovery increases on addition of methanol as co-solvent, which is primarily attributed to the increase in yield of bio-crude. Nearly two times improvement in energy recovery is recorded with experiment R13 as compared to R4. This shows that the addition of methanol and the homogeneous catalyst play a vital role. The ECR provides an estimate of the effectiveness of the HTL process compared to the energy that can be recovered by combustion of bio-crude. ECR value greater than unity signifies that the process consumes more energy than that generated in the bio-crude, and vice versa when ECR is lower than unity. Therefore, $ECR < 1.0$ is preferred. It is evident from Table 6 that, with only water as the solvent,

ECR is 2.03. This shows that the process may not be favorable from an energy perspective. However, with the addition of methanol and the catalyst, a net-positive energy balance is obtained. It can be concluded that both the processes (addition of methanol and catalyst) are energetically feasible. A particular advantage of adding methanol as a co-solvent is reflected in the low energy required to raise the temperature of the slurry to the required temperature, as compared to using only water as the solvent. In addition to the energy advantage, the addition of co-solvent also improves the yield of the bio-crude, which is reflected in energy recovery, which is nearly two times higher as compared to that using only water. These are comparable with HTL of microalgae and defatted microalgae, and certainly better than that of pyrolysis bio-oil [47]. An ensemble of the results demonstrates that HTL, using methanol as a co-solvent, is a promising thermochemical technology to convert the abundantly available waste rice straw to valuable bio-crude with low oxygen content and high HHV.

Table 6. Energy calculations to determine energy recovery and ECR in HTL of rice straw at 300 °C, 60 min, and rice straw:solvent ratio of 1:10 wt./wt.

	Water	Water:Methanol 50:50 (Vol.%/Vol.%)	Water:Methanol 50:50 (Vol.%/Vol.%) + KOH
Energy content of rice straw (E_F) (kJ)	363	363	363
Heat of rice straw (Q_{RS}) (kJ)	6.93	6.93	6.93
Heat of water (Q_{H_2O}) (kJ)	362.62	181.30	181.30
Heat of methanol ($Q_{Methanol}$) (kJ)	-	32.65	32.65
Heat required for HTL process (E_{HTL}) (kJ)	263.96	157.80	157.80
Total energy of products (E_P) (kJ):	322.62	424.50	478.34
Energy recovered in bio-crude (kJ)	130.26	305.00	387.83
Energy recovered in bio-char (kJ)	137.64	64.75	35.79
Energy recovered in gases (kJ)	54.72	54.72	54.72
$E_F + Q_{solvent}$ (kJ)	725.62	576.96	576.96
Energy recovery (ER) (%)	44.5	73.6	82.9
Energy consumption ratio (ECR)	2.03	0.52	0.41

4. Conclusions

Through a series of systematic experiments, a better-quality bio-crude was obtained from rice straw at 300 °C, 18 MPa, and a 60 min processing time, using only water as the solvent at rice straw:water ratio of 1:10 (wt./wt.). At this condition, the bio-crude yield was 12.3 wt.%, HHV was 35.3 MJ kg⁻¹, oxygen content was 14.2 wt.%, and energy recovery was 36%. The major organic constituents in the bio-crude were phenolic compounds, cyclo-oxygenates like cyclopentenone and its derivatives, and other aromatics. The selectivities to phenolic compounds, cyclopentenone, and its derivatives and aromatics at this condition were 50%, 18%, and 21%, respectively. In order to further improve the yield and quality of bio-crude, methanol was used as a co-solvent. The yields of bio-crude increased up to 36.8 wt.% with the addition of methanol in equal volume ratio with water. The oxygen content and HHV of bio-crude were 17.8 wt.% and 32.8 MJ kg⁻¹, respectively. Esters emerged as the major constituents of bio-crude, owing to the enhancement of esterification reactions under acid/base-catalyzed conditions in presence of methanol:water. The addition of alkali catalysts further improved the yield of bio-crude, with a maximum yield of ~40 wt.% obtained using 5 wt.% KOH. The catalysts promoted both hydrolytic cleavage of biomass components to produce phenolics and cyclo-oxygenates, and esterification reactions to produce methyl esters. Energy recovery was calculated to be in the range of 70%–80% for HTL conducted in presence of methanol:water. The energy-consumption ratio was lesser than unity for the methanol:water system, suggesting that the process produced more energy in the bio-crude than it consumed.

This study proves that recovery of valuable esters may be targeted from HTL bio-crude for their use in various industries, such as soap manufacturing, cosmetics, food, detergents, and chemicals. Moreover, an analysis of the energy-consumption ratio for the presented scenarios in a continuous

HTL process with energy integration among multiple unit operations, and a detailed study on the techno-economic aspects are essential to establish the commercial viability of the HTL technology for biomass agro residue valorization.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1996-1073/13/10/2618/s1>. Figure S1: Temperature and pressure profiles from selected experiments performed at rice-straw-to-water ratio of 1:10 wt./wt. Tables S1–S10: Detailed composition of bio-crude from experiments R1, R2, R4, R5, R10, R11, R12, R13, R14 and R15, respectively. S11: Sample calculation to determine energy recovery (%) and ECR.

Author Contributions: Conceptualization, A.Y., R.V., and S.R.C.; methodology and validation, A.Y., A.K.S.V., and S.S.; formal analysis, investigation, data curation, writing—original draft preparation, and writing—review and editing, A.Y. and R.V.; resources, supervision, project administration, and funding acquisition, R.V. and S.R.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the DEPARTMENT OF SCIENCE AND TECHNOLOGY (DST), INDIA, in the form of a grant to National Center for Combustion Research and Development at Indian Institute of Technology Madras.

Conflicts of Interest: The authors declare no conflict of interest.

References

- McLaughlin, O.; Mawhood, B.; Jamieson, C.; Slade, R. Rice straw for bioenergy: The effectiveness of policymaking and implementation in Asia. In Proceedings of the 24th European Biomass Conference and Exhibition, Amsterdam, The Netherlands, 6–9 June 2016; pp. 1540–1554. [CrossRef]
- Sarma, S.D. Paddy Residue Burning: Drivers, Challenges and Potential Solutions. Available online: <http://www.teriin.org/article/paddy-residue-burning-drivers-challenges-and-potential-solutions> (accessed on 20 March 2020).
- Nanda, S.; Mohammad, J.; Reddy, S.N.; Kozinski, J.A.; Dalai, A.K. Pathways of lignocellulosic biomass conversion to renewable fuels. *Biomass. Conv. Bioref.* **2014**, *4*, 157–191. [CrossRef]
- Zhou, X.; Broadbelt, L.J.; Vinu, R. Mechanistic understanding of thermochemical conversion of polymers and lignocellulosic biomass. In *Advances in Chemical Engineering: Thermochemical Process Engineering*; Van Geem, K., Ed.; Elsevier: Amsterdam, The Netherlands, 2016; Volume 49, pp. 95–198.
- Tekin, K.; Karagöz, S.; Bektaş, S. A review of hydrothermal biomass processing. *Renew. Sustain. Energy Rev.* **2014**, *40*, 673–687. [CrossRef]
- Peterson, A.A.; Vogel, F.; Lachance, R.P.; Froling, M.; Antal, J.M.J.; Tester, J.W. Thermochemical biofuel production in hydrothermal media: A review of sub and supercritical water technologies. *Energy Environ. Sci.* **2008**, *1*, 32–65. [CrossRef]
- Toor, S.S.; Rosendahl, L.; Rudolf, A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* **2011**, *36*, 2328–2342. [CrossRef]
- Liu, Z.; Zhang, F.S. Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks. *Energy Convers. Manag.* **2008**, *49*, 3498–3504. [CrossRef]
- Wang, Y.; Wang, H.; Lin, H.; Zheng, Y.; Zhao, J.; Pelletier, A.; Li, K. Effects of solvents and catalysts in liquefaction of pinewood sawdust for the production of bio-crudes. *Biomass Bioenergy* **2013**, *59*, 158–167. [CrossRef]
- Zhu, W.W.; Zong, Z.M.; Yan, H.L.; Zhao, Y.P.; Lu, Y.; Wei, X.Y.; Zhang, D. Cornstalk liquefaction in methanol/water mixed solvent. *Fuel Process. Technol.* **2014**, *117*, 1–7. [CrossRef]
- Piñkowska, H.; Wolak, P.; Złocińska, A. Hydrothermal decomposition of alkali lignin in sub- and supercritical water. *Chem. Eng. J.* **2012**, *187*, 410–414. [CrossRef]
- Yuan, Z.; Cheng, S.; Leitch, M.; Xu, C. Hydrolytic degradation of alkaline lignin in hot-compressed water and ethanol. *Bioresour. Technol.* **2010**, *101*, 9308–9313. [CrossRef]
- Malins, K.; Kampars, V.; Brinks, J.; Neibolte, I.; Murnieks, R.; Kampare, R. Bio-crude from thermo-chemical hydro-liquefaction of wet sewage sludge. *Bioresour. Technol.* **2015**, *187*, 23–29. [CrossRef]
- Zhang, B.; Keitz, M.; Valentas, K. Thermal effects on hydrothermal biomass liquefaction. *Appl. Biochem. Biotechnol.* **2008**, *147*, 143–150. [CrossRef] [PubMed]
- Wei, N.; Via, B.K.; Wang, Y.; McDonald, T.; Auad, M.L. Liquefaction and substitution of switchgrass (*Panicum virgatum*) based bio-crude into epoxy resins. *Ind. Crop. Prod.* **2014**, *57*, 116–123. [CrossRef]

16. Valdez, P.J.; Savage, P.E. A reaction network for the hydrothermal liquefaction of *Nannochloropsis* sp. *Algal. Res.* **2013**, *2*, 416–425. [CrossRef]
17. Valdez, P.J.; Tocco, V.J.; Savage, P.E. A general kinetic model for the hydrothermal liquefaction of microalgae. *Bioresour. Technol.* **2014**, *163*, 123–127. [CrossRef]
18. Yuan, X.Z.; Li, H.; Zeng, G.M.; Tong, J.Y.; Xie, W. Sub- and supercritical liquefaction of rice straw in the presence of ethanol-water and 2-propanol-water mixture. *Energy* **2007**, *32*, 2081–2088. [CrossRef]
19. Li, H.; Yuan, X.; Zeng, G.; Tong, J.; Yan, Y.; Cao, H.; Wang, L.; Cheng, M.; Zhang, J.; Yang, D. Liquefaction of rice straw in sub- and supercritical 1,4-dioxane-water mixture. *Fuel Process. Technol.* **2009**, *90*, 657–663. [CrossRef]
20. Singh, R.; Chaudhary, K.; Biswas, B.; Balagurumurthy, B.; Bhaskar, T. Hydrothermal liquefaction of rice straw: Effect of reaction environment. *J. Supercrit. Fluids* **2015**, *104*, 70–75. [CrossRef]
21. Zhou, C.; Zhu, X.; Qian, F.; Shen, W.; Xu, H.; Zhang, S.; Chen, J. Catalytic hydrothermal liquefaction of rice straw in water/ethanol mixtures for high yields of monomeric phenols using reductive CuZnAl catalyst. *Fuel Process. Technol.* **2016**, *154*, 1–6. [CrossRef]
22. Cao, L.; Zhang, C.; Hao, S.; Luo, G.; Zhang, S.; Chen, J. Effect of glycerol as co-solvent on yields of bio-crude from rice straw through hydrothermal liquefaction. *Bioresour. Technol.* **2016**, *220*, 471–478. [CrossRef]
23. Castello, D.; Pedersen, T.H.; Rosendahl, L.A. Continuous hydrothermal liquefaction of biomass: A critical review. *Energies* **2018**, *11*, 3165. [CrossRef]
24. Brand, S.; Kim, J. Liquefaction of major lignocellulosic biomass constituents in supercritical ethanol. *Energy* **2015**, *80*, 64–74. [CrossRef]
25. Saraswat, V.K.; Bansal, R. India's Leapfrog to Methanol Economy. Available online: http://niti.gov.in/writereaddata/files/document_publication/Article%20on%20Methanol%20Economy_Website.pdf (accessed on 20 March 2020).
26. ASTM E1131-08. Standard Test Method for Compositional Analysis by Thermogravimetry. Available online: <http://www.astm.org/Standards/E1131.htm> (accessed on 20 March 2020).
27. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. An overview of the chemical composition of biomass. *Fuel* **2010**, *89*, 913–933. [CrossRef]
28. Chopra, J.; Mahesh, D.; Yerrayya, A.; Vinu, R.; Rajnish, K.; Sen, R. Performance enhancement of hydrothermal liquefaction for strategic and sustainable valorization of de-oiled yeast biomass into green bio-crude. *J. Clean. Prod.* **2019**, *227*, 292–301. [CrossRef]
29. Run-dong, L.; Bing-shuo, L.; Tian-hua, Y.; Ying-hui, X. Liquefaction of rice stalk in sub- and supercritical ethanol. *J. Fuel Chem. Technol.* **2013**, *41*, 1459–1465.
30. Francis, H.E.; Lloyd, W.G. Predicting heating value from elemental composition. *J. Coal Qual.* **1983**, *2*, 2.
31. Nam, H.; Capareda, S.C.; Ashwath, N.; Kongkasawan, J. Experimental investigation of pyrolysis of rice straw using bench-scale auger, batch and fluidized bed reactors. *Energy* **2015**, *93*, 2384–2394. [CrossRef]
32. Tsai, W.T.; Lee, M.K.; Chang, Y.M. Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. *J. Anal. Appl. Pyrol.* **2006**, *76*, 230–237. [CrossRef]
33. Akhtar, J.; Amin, N.A.S. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renew. Sustain. Energy Rev.* **2011**, *15*, 1615–1624. [CrossRef]
34. Pedersen, T.H.; Jasiūnas, L.; Casamassima, L.; Singh, S.; Jensen, T.; Rosendahl, L.A. Synergetic hydrothermal co-liquefaction of crude glycerol and aspen wood. *Energy Convers. Manag.* **2015**, *106*, 886–889. [CrossRef]
35. Feng, S.; Wei, R.; Leitch, M.; Xu, C.C. Comparative study on lignocellulose liquefaction in water, ethanol, and water/ethanol mixture: Roles of ethanol and water. *Energy* **2018**, *155*, 234–241. [CrossRef]
36. Panagiotopoulou, P.; Vlachos, D.G. Liquid phase catalytic transfer hydrogenation of furfural over a Ru/C catalyst. *Appl. Catal. A Gen.* **2014**, *480*, 17–24. [CrossRef]
37. Li, H.; Yuan, X.; Zeng, G.; Huang, D.; Huang, H.; Tong, J.; You, Q.; Zhang, J.; Zhou, M. The formation of bio-oil from sludge by deoxy-liquefaction in supercritical ethanol. *Bioresour. Technol.* **2010**, *101*, 2860–2866. [CrossRef] [PubMed]
38. Sing, S.K.; Ekhe, J.D. Towards effective lignin conversion: HZSM-5 catalysed one-pot solvolytic depolymerisation/ hydrodeoxygenation of lignin into value added compounds. *RSC Adv.* **2014**, *4*, 27971–27978. [CrossRef]
39. Tekin, K.; Karagöz, S. Non-catalytic and catalytic hydrothermal liquefaction of biomass. *Res. Chem. Intermed.* **2013**, *39*, 485–498. [CrossRef]

40. Minowa, T.; Kondo, T.; Sudirjo, S.T. Thermochemical liquefaction of Indonesian biomass residues. *Biomass Bioenergy* **1998**, *14*, 517–524. [[CrossRef](#)]
41. Zhu, Z.; Toor, S.S.; Rosendahl, L.; Yu, D.; Chen, G. Influence of alkali catalyst on product yield and properties via hydrothermal liquefaction of barley straw. *Energy* **2015**, *80*, 284–292. [[CrossRef](#)]
42. Singh, R.; Prakash, A.; Dhiman, S.K.; Balagurumurthy, B.; Arora, A.K.; Puri, S.K.; Bhaskar, T. Hydrothermal conversion of lignin to substituted phenols and aromatic ethers. *Bioresour. Technol.* **2014**, *165*, 319–322. [[CrossRef](#)]
43. Pelzer, A.W.; Sturgeon, M.R.; Yanez, A.J.; Chupka, G.; O'Brien, M.H.; Katahira, R.; Cortright, R.D.; Woods, L.; Beckham, G.T.; Broadbelt, L.J. Acidolysis of α -O-4 aryl-ether bonds in lignin model compounds: A modeling and experimental study. *ACS Sustain. Chem. Eng.* **2015**, *3*, 1339–1347. [[CrossRef](#)]
44. Liu, A.; Park, Y.; Huang, Z.L.; Wang, B.W.; Ankumah, R.O.; Biswas, P.K. Product identification and distribution from hydrothermal conversion of walnut shells. *Energy Fuels* **2006**, *20*, 446–454. [[CrossRef](#)]
45. Cheng, S.; D'cruz, I.; Wang, M.C.; Leitch, M.; Xu, C.B. Highly efficient liquefaction of woody biomass in hot-compressed alcohol-water co-solvents. *Energy Fuels* **2010**, *24*, 4659–4667. [[CrossRef](#)]
46. Yokoyama, S.; Suzuki, A.; Murakami, M.; Ogi, T.; Koguchi, K.; Nakamura, E. Liquid fuel production from sewage sludge by catalytic conversion using sodium carbonate. *Fuel* **1987**, *66*, 1150–1155. [[CrossRef](#)]
47. Vardon, D.R.; Sharma, B.K.; Grant, V.B.; Rajagopalan, K. Thermochemical conversion of raw and defatted algal biomass via hydrothermal liquefaction and slow pyrolysis. *Bioresour. Technol.* **2012**, *109*, 178–187. [[CrossRef](#)] [[PubMed](#)]



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