

Article

New Insights for the Future Design of Composites Composed of Hydrochar and Zeolite for Developing Advanced Biofuels from Cranberry Pomace

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Abstract: This study provides fundamental insight and offers a promising catalytic hydrothermal method to harness cranberry pomace as a potential bioenergy and/or hydrochar source. The physical and chemical properties of Canadian cranberry pomace, supplied by Fruit d'Or Inc., were examined and the optimum operational conditions, in terms of biocrude yield, were obtained by the I-optimal matrix of Design Expert 11. Afterward, cranberry pomace hydrochar (CPH) and zeolite were separately introduced to the hydrothermal liquefaction (HTL) process to investigate the benefits and disadvantages associated with their catalytic activity. CPH was found to be a better host than zeolite to accommodate cellulosic sugars and showed great catalytic performance in producing hydrocarbons. However, high amounts of corrosive amino and aliphatic acids hinder the practical application of CPH as a catalyst. Alternatively, zeolite, as a commercial high surface area catalyst, had a higher activity for deoxygenation of compounds containing carbonyl, carboxyl, and hydroxyl groups than CPH and resulted in higher selectivity of phenols. Due to the low hydrothermal structural stability, coke formation, and narrow pore size distribution, further activations and modifications are needed to improve the catalytic behavior of zeolite. Our results suggest that a composite composed of CPH and zeolite can resolve the abovementioned limitations and help with the development and commercialization of advanced biofuels from cranberry pomace.

Keywords: hydrothermal liquefaction; cranberry pomace; fruit processing; catalyst; composite

1. Introduction

Fruit processing industries in the world produce approximately 38.1 million metric tonnes (Mt) of fruit waste. This remarkable amount of waste is gaining significant interest as a sustainable and second-generation biofuel source [1]. Canada produces more than 25% of the world's cranberries, making the country the second-largest cranberry producer in the world. Cranberry pomace, as a major by-product of juice processing, is normally directly discarded or, in the best-case scenario, used as animal feed or composted along with the other municipal organic wastes [2]. These disposal methods have been found to be a threat to the environment and human health. Due to the mentioned consequences along with the depletion of fossil fuels, global warming, and eutrophication, the development of an innovative method to process fruit waste is now a high priority worldwide [3]. Although huge efforts were made to introduce fruit waste as an organic input of biogas plants, it cannot be simply digested by conventional anaerobic digestion processes due to its poor cellulose content which limits methanogenic processes [4]. However, fruit wastes have a moisture content of approximately 70%

and contain various hydrothermally degradable compounds (e.g., fiber, protein, and reducing sugars), which make it suitable to be used as a feedstock in the hydrothermal liquefaction (HTL) method [5]. For example, Anouti et al. analyzed the oil derived from the HTL of blackcurrant pomace with standard normalized tests and compared its products with the specifications needed for conventional fuels. The results showed that blackcurrant pomace oil cannot yet be used as a commercially tradable product [6]. The key to reaching high yield and quality hydrocrude by HTL process is in designing and using suitable catalysts. To date, the most studied and potentially important heterogeneous catalysts are Pd, Pt, Fe, Ni, Co, Ru, and other metals supported on zeolite, which is still suffering from disadvantages such as producing higher amounts of aromatics, heavy products, and cokes [7–9]. Therefore, the variety of post-synthetic modification protocols for zeolites have been studied [10]. Concurrently, the use of hydrochar as a precursor of composite materials has been an increasing trend in recent years [11]. Hydrochar-based composites made from the physical and chemical addition of metal oxides, zeolites, nano carbons (i.e., carbon nanotubes, carbon nanofibers, graphene, and carbon nitride), and polymers (i.e., polyaniline, polypyrrol, and polythiophene) have been developed for use in various energy conversion and storage systems [12–16]. It is believed that the three-dimensional (3D) structure of modified hydro/biochar uses the interconnected structure as channels for increasing the density of reactants by creating a locally higher pressure [17]. This study provides considerable insight into the necessity of producing a composite made from cranberry pomace hydrochar (CPH) and commercial zeolite. To the best of our knowledge, no study has been conducted on petroleum hydrocarbon fractions production (biodiesel, light gasoline, and gasoline) from cranberry pomace using HTL and no investigation has compared the effect of hydrochar and zeolite as a catalyst on the functional groups in the bio-oil portion.

This paper includes three main parts intending to develop advanced biofuel from cranberry pomace. First, before conducting any experiments, the physical and chemical properties of cranberry pomace supplied by Fruit d’Or Inc. were presented and discussed for the estimation of potential biofuel production in the HTL process. Then optimum operational conditions were investigated by the I-optimal matrix of Design Expert 11 for reaching a maximum yield of hydrocrude. Finally, catalytic HTL tests were performed under the optimum condition. To this end, two different catalysts, hydrochar and zeolite, were separately introduced in the HTL of cranberry pomace in a 300 mL Parker Hastelloy high-pressure reactor. The results provide fundamental insight and offer an important guideline for the future design of a composite composed of hydrochar and zeolite to take advantage of both catalytic behaviors.

Our hypothesis is that a catalyst based on hydrochar and zeolite (hydrochar/zeolite composite) can resolve present limitations and challenges for developing and commercializing advanced biofuels such as biodiesel and bio-gasoline by:

- Creating meso/macropores into the micropores structure of the zeolite;
- Increasing the number of accessible active sites for macromolecules;
- Enhancing the thermal stability of the zeolite;
- Creating 3D interconnected structure using activated hydrochar.

2. Material and Methods

2.1. Feedstock and Chemicals

Cranberry pomace used in this study was kindly supplied by Fruit d’Or. Samples were collected and immediately stored in the fridge at +4 °C. The cranberry pomace sample was analyzed for moisture using AACC-method 44-15.02. Soluble and insoluble dietary fiber and total starch were quantified using Megazyme® Integrated Total Dietary Fiber and Total Starch HK kits, respectively (Megazyme, Wicklow, Ireland). Reducing sugars, extractable phenolics (EPP, which are extracted with aqueous-organic solvents), hydrolyzable phenolic compounds (HPP, low molecular weight phenolic compounds that need an acid hydrolysis to be extracted because they are bounded to the cell wall) and nonextractable

proanthocyanidins (NEPA, proanthocyanidins that cannot be extracted with aqueous-organic solvents and need an acid hydrolysis at high temperatures), were analyzed as reported in detail in Pico et al. [18]. Particle size was determined in triplicate using a Mastersizer 2000 laser diffraction particle size analyzer from Malvern Instruments (Worcestershire, UK). Last, crude protein content was determined following AACC 46-30.01 using an automatic elemental analyzer (Leco, St. Joseph, MO, USA) for the analysis of nitrogen, using the factor of 6.25 to convert the measured nitrogen into protein. Briefly, the cranberry used in the study has a total moisture content, protein content, reducing sugars, and extractable phenolics (EPP) of $13 \pm 0.53\%$, $4.29 \pm 0.02\%$, $6.34 \pm 0.01\%$, and 2415.97 ± 66.57 (mg/100 g, FBBB, $n = 12$), respectively. Table 1 gives the composition and elemental analysis of the biomass used in this study

Table 1. Physical and chemical properties of cranberry pomace supplied by Fruit d’Or Inc.

Parameters	Cranberry	±
Moisture content (%)	13.00	0.53
Particle size (D 4.3)	286.85	2.28
Protein content (%)	4.29	0.02
TDF_IDF (%)	72.71	0.81
TDF_SDFP (%)	11.97	0.22
Total starch (%)	no	
Reducing sugars (%)	6.34	0.01
EPP (mg/100 g)	1210.11	143.43
HPP (mg/100)	2000.41	210.44
NEPA anthocyanidins (mg/100 g)	161.52	10.31
DPPH EPP (IC50)	2.52	0.21
DPPH HPP (IC50)	0.56	0.01
DPPH NEPA (IC50)	0.16	0.01
Carbon (%)	50.69	0.09
Hydrogen (%)	6.88	0.03
Nitrogen (%)	0.92	0.03
Oxygen (%)	45.86	0.12
Calcium (%)	0.05	0.01
Magnesium (%)	0.04	0.002
Potassium (%)	0.24	0.03

2.2. Hydrothermal Liquefaction Experiments

To perform the HTL experiments, a stirred reactor with 300 mL capacity, from Parker Hannifin Corporation, USA was utilized. The material of the inside of the reactor is Hastelloy, which minimizes contamination during experiments. Moreover, it benefits from a temperature controller that is equipped with a cooling loop, allowing fast-response temperature alignment.

A mixture of 5 g of the sample by dry-basis and 25 g of water was introduced to the reactor for each experiment. Nitrogen gas was passed through the reactor to purge it from air, and then used to pressurize the reactor’s contents to ensure the experiments were held below the saturation temperature of water. The heating jacket around the reactor was used to increase the temperature of the reactor’s contents to the setpoint of the experiments (300, 325 and 350 °C). After holding the reactor at the setpoint temperature for the specific residence time of each experiment (5, 20 and 35 min), it was quickly cooled down to below 30 °C by switching off the heater and using the cooling loop inside the reactor.

To quantify the mass yield of the gas phase, the gas inside of the reactor was collected by connecting the reactor's outlet valve to a graduated cylinder that was previously filled with water. The volume of the initial nitrogen gas was then subtracted from the volume of the collected gas to find the volume of the produced gas due to the reactions. The mass of the produced gas was then calculated assuming that it is only composed of CO₂. Finally, the gas yield was obtained by dividing the mass of the produced gas by the initial mass of the sample. The liquid-hydrochar mixture was collected from the reactor and separated using a filter paper. The solid portion was dried in a furnace at 105 °C overnight. The hydrochar yield was then calculated by dividing the weight of the dried hydrochar by the weight of the initial sample. Finally, the liquid yield was calculated by subtracting the sum of solid and gas yield from 100%.

2.3. Characterization of Bioproducts

2.3.1. Py-GCMS Analysis

The liquid portions obtained from the HTL experiments were sent to a Frontier LAB pyrolyzer connected to an Agilent Technology 7890B GC and the Agilent 240 Ion Trap mass spectrometer (MS) (Agilent Technologies, California, CA, USA) for further analysis. A U-shape quartz tube was used to place samples with an approximate weight of 0.2–0.4 mg. Single-shot flash pyrolysis was carried out with a 20 °C/ms heating rate, 300 °C setpoint temperature, and 20 s residence time. The flow rate and split ratio of helium as the carrier gas were 20 mL/min and 20:1, respectively. The pyrolysis products were separated in the Agilent HP-5 ms column (30 m × 0.25 mm i.d., film thickness 0.25 µm). The temperature for the mass spectrometer ion source and the interface were adjusted at 230 and 300 °C, respectively, and scanning was conducted once per second in the range of 0–550 *m/z*. NIST mass spectral database versions 147 and 27 with an identity threshold cut-off of 50 were used to identify the peaks. Qualitative Analysis 10.0 Software could then integrate and identify the peaks and sort them with respect to the peak area percentage at the corresponding retention time. The name of the compounds, their structure, and their molecular formula was found by using the F-search tool of the system. The main constituents in the pyrolysis vapor were specified by a semiquantitative study by peak area % of each PyC.

2.3.2. BET Analysis

Quantachrome 4200e Surface Area and Pore Analyzer were used for the BET tests. The samples were introduced in the degassing module of the analyzer for 3 h, prior to the BET analysis. Next, the samples were reweighed to find the mass loss, and then they were placed in the analyzer for multipoint BET analysis. By recording the volume of the adsorbate gas (nitrogen) at −196 °C, and relative pressures ranging from 0.05 < *P*/*P*₀ < 0.97, the adsorption isotherm of each sample was obtained. The isotherm was analyzed with the incorporated software of the BET machine to find the targeted parameters such as specific surface area, pore-volume, and pore diameter of each sample.

3. Results and Discussion

3.1. Optimization of Operating Parameters for Maximum Yield of Biocrude

To obtain the optimum operational condition, the effects of two main parameters in HTL including temperature and time on the responses including hydrochar, gas, biocrude, and aqueous phase yields were investigated by the I-optimal matrix of Design Expert 11. Fourteen experiments were performed as described in Table 2. The HTL process was carried out at temperatures ranging between 300 and 350 °C for 5, 20, and 35 min. The optimization method used in this study was similar to that described in our previous work [19].

As shown in Figure 1a, by increasing the temperature from 300 to 350 °C and time from 5 to 35 min, the hydrochar yield experienced a significant decrease. The lowest hydrochar yield is related

to a temperature of 350 °C, and residence time of around 35 min. This indicates the conversion of biochemicals into biocrude or other phases. The biocrude yield (Figure 1b) shows a sharp increase with an increase in the process temperature, up to around 325 °C. After this temperature, the yield decreases significantly in higher residence times. The highest yield of the biocrude is around 34.98%, which can be attributed to the temperature of 350 °C and residence times of 35 min. This phenomenon is due to the improved self-ionization of water in which $[H^+]$ and $[OH^-]$ would liquefy large molecules present in the CP into smaller compounds. Figure 1c demonstrates the aqueous phase yield versus the binary combination of temperature and time. In this diagram, changes in the inserted variables lead to aqueous phase yield varying from 33.03 to 36.19 wt%. Figure 1d shows the gas yield versus the binary combination of time and temperature. In this diagram, it is shown that by increasing both temperature and time, the gas yield increased from 10.07 to 14.19 wt%. Obviously, this is due to the higher gasification at higher severity. Since the present study aimed to find the highest yield of biocrude with minimal operational temperature, the temperature of 325 °C and retention time of 35 min was considered as the optimal operating condition for performing catalytic HTL. The results are in agreement with the literature [20].

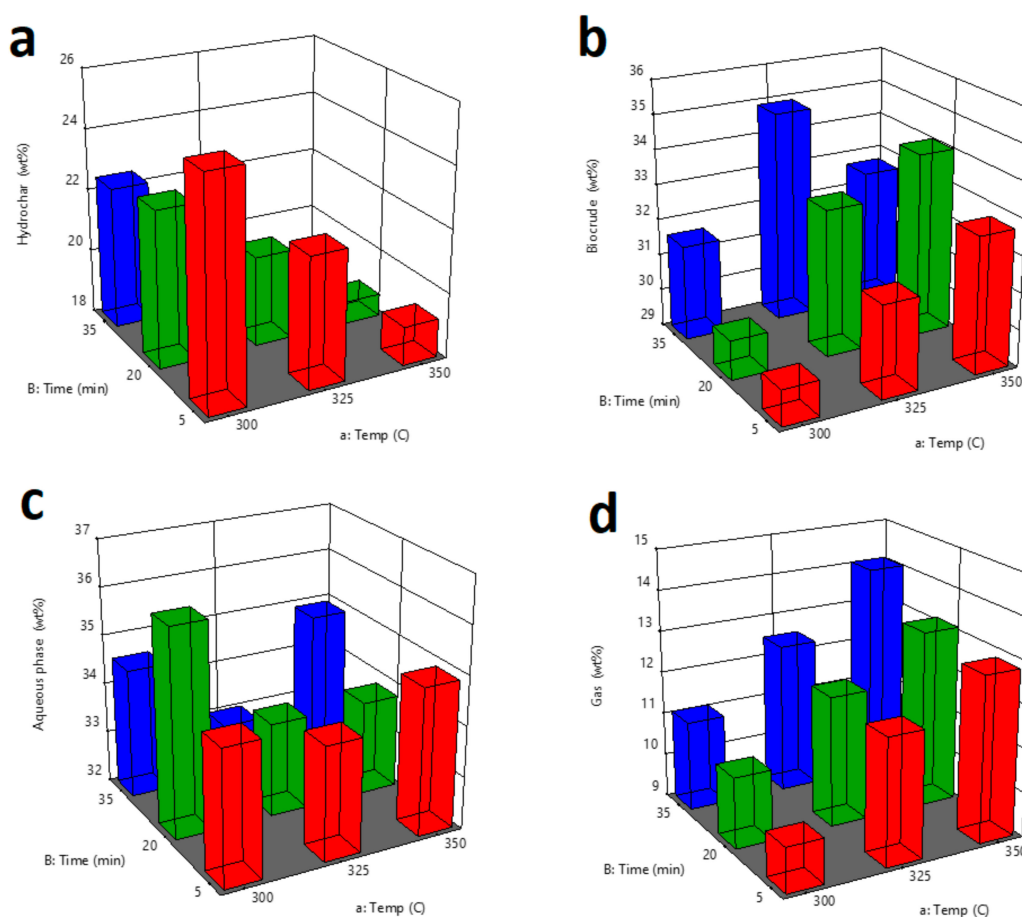


Figure 1. Effect of operating parameters on (a) hydrochar yield, (b) biocrude yield, (c) aqueous phase yield, and (d) gas yield.

Table 2. Design of experiments by the I-optimal matrix of Design Expert 11.

Run	a:Temp	B:Time	Hydrochar	Biocrude	Aqueous Phase	Gas
	C	min	wt%	wt%	wt%	wt%
1	325	35	19.47	34.90	33.03	12.60
2	325	20	20.98	33.09	33.80	12.13
3	350	35	18.16	33.01	34.82	14.01
4	350	20	18.69	34.19	34.02	13.10
5	350	5	19.21	32.80	35.11	12.88
6	325	20	20.80	33.15	33.98	12.07
7	325	35	19.40	34.98	33.07	12.55
8	325	5	22.14	31.59	34.29	11.98
9	350	5	19.28	32.87	34.85	13.00
10	350	20	18.77	34.12	33.78	13.33
11	350	35	18.11	32.55	35.15	14.19
12	300	5	25.22	30.00	34.71	10.07
13	300	35	22.56	31.68	34.62	11.14
14	300	20	23.01	30.11	36.19	10.69

3.2. Chemicals Identified Based on Their Functional Groups

More than 120 compounds were detected through Frontier LAB pyrolyzer connected to an Agilent Technology 7890B GC. To achieve a better understanding of the biocrude product releasing from catalytic HTL of cranberry pomace, an in-depth investigation on acids, nitrogen compounds, ketones, aldehydes, furans, phenols, alcohols, hydrocarbons, and esters was conducted for three different scenarios: noncatalyst, hydrochar, and zeolite.

The selectivity of the functional groups is depicted in Figure 2. As the weight percentage of the biocrude in all scenarios (noncatalyst, hydrochar, and zeolite) was the same, the corresponding peak of any specific component in the biocrude, can be used to compare its concentration in different scenarios [21,22]. As shown in Figure 2 and Table S1, in noncatalytic HTL, organic acids (i.e., benzoic acid, oleic acid, palmitic acid, glutamic acid, and stearic acid) and furans (i.e., 2-Furfural, 5-Methylfuran-2(3H)-one, 5-Hydroxymethylfurfural) are the main components, the majority of which are derived from the initial fragmentation of the C6 sugars like fructose and glucose [23]. In general, small carbonyl and cellulose-derived compounds are the most prevalent compounds detected in the biocrude derived from noncatalytic experimentation. In catalytic HTL of cranberry, lignin-derived compounds such as guaiacol, catechol, 3-Methylcatechol, and p-vinylphenol were produced in significant quantity. For the zeolite, the main functional groups are phenols (25.19%), which agrees with the literature. Experimental studies on catalytic HTL over various zeolite-based catalysts indicated that zeolites are the most effective catalyst for phenol production [24]. This phenomenon is due to the better degradation of furfural intermediates into phenol over the acidic surface of zeolite [25]. Hydrochar showed high selectivity for hydrocarbons (16.34%). The main reactions by which hydrocarbons are produced include hydrogenation, deoxygenation, etherification, different C–C formation reactions (e.g., aldol condensation, hydroxyalkylation, alkylation, and optional combinations) of the hydroxymethylfurfural (HMF) and furfural obtained from chemical dehydration of hexoses and pentoses [26]. Therefore, it can be concluded that further modification is needed for the zeolite to make it a suitable catalyst for macro-molecules and simultaneously increase hydrocarbon content. This study provides fundamental insights for synthesizing a catalyst composed of both hydrochar and zeolite to take advantage of both catalytic behaviors.

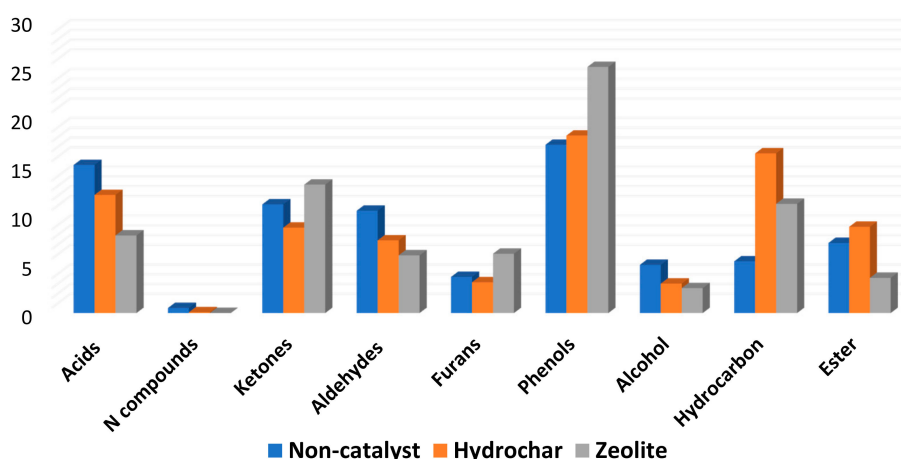


Figure 2. In-depth investigation of biocrude in terms of functional groups.

3.3. Decomposition Indicators in the HTL Process

Among all those chemicals detected by GCMS, carbon dioxide and levoglucosan have been selected as two important indicators of decarboxylation and decomposition. Usually when zeolites are used as a catalyst in the HTL process, most of the thermally produced oxygenates primarily go through decarbonylation to form reaction intermediates, which subsequently will be converted into aromatics over the zeolite catalyst [27]. This phenomenon confirms the higher selectivity of phenols (25.19%) in zeolite than that from hydrochar (18.16%). Therefore, as can be seen in Figure 3, the selectivity of carbon dioxide for zeolite hydrocrude (4.99%) is lower than hydrochar hydrocrude (7.17%), showing fewer oxygenates in hydrocrude when the zeolite is used as a catalyst.

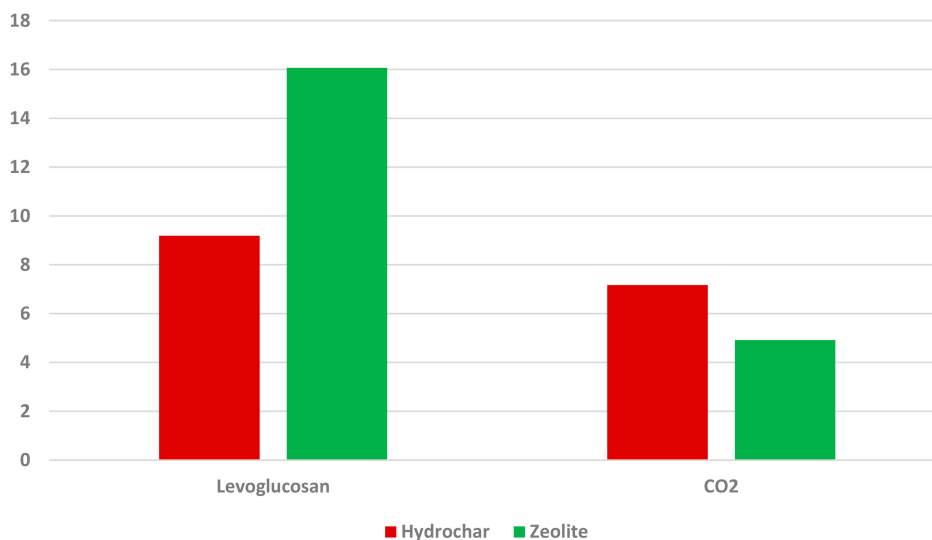


Figure 3. Two important indicators in HTL in terms of selectivity (%).

Levoglucosan is the most prevalent sugar derived from cellulose. The selectivity of levoglucosan decreased significantly in both cases where catalysts were used, which is in agreement with previous experimental observations [28–30]. The hierarchically porous carbon derived from cranberry could potentially be a better host than zeolite to accommodate cellulosic sugars.

3.4. Hydrocarbon Fractions in the Biocrude

Many researchers are looking for a novel approach or mechanism to produce the greatest yield of fuel fractions, including light gasoline, heavy gasoline, and biodiesel from biomass. According to the literature, Ketonization is the most important reaction by which the carboxylic functional groups are removed, while simultaneously increasing the size of the carbon chain. The aldol condensation of ketones and oligomerization of alkenes are responsible for producing molecules within the range of fuel-sized molecules fuel molecular size range [21,26,28]. As it can be seen in Figure 4, the selectivity of light gasoline (C5–C6) in the upgraded bio-oil is in the order of noncatalyst > zeolite > hydrochar. It should be noted that the gasoline fraction hydrocarbons in noncatalytic HTL are mostly acids and furans, therefore, it is a nonstable product with low energy content. Zeolite catalysts showed superior activity towards gasoline (C7–C12) compared to that of a hydrochar catalyst. The selectivity for gasoline is in the order of zeolite > hydrochar > noncatalyst. The heavy gasoline in zeolite is mainly composed as a mixture of phenols and ketones. Hydrochar showed great catalytic performance in producing biodiesel range hydrocarbons which make it a promising candidate for producing high quality drop-in biofuel. However, high amounts of corrosive amino and aliphatic acids hinder the practical application of solely using hydrochar as a catalyst. We believe that the results provide new insights for catalytic HTL and emphasize on the necessity of producing a composite, composed of hydrochar and zeolite. Our hypothesis about the catalytic effect of hydrochar and zeolite relies on the combination of different catalytic effects in hydrochar and zeolite. Figure 5 summarizes the key advantages and disadvantages of hydrochar, and zeolite derived from the current study.

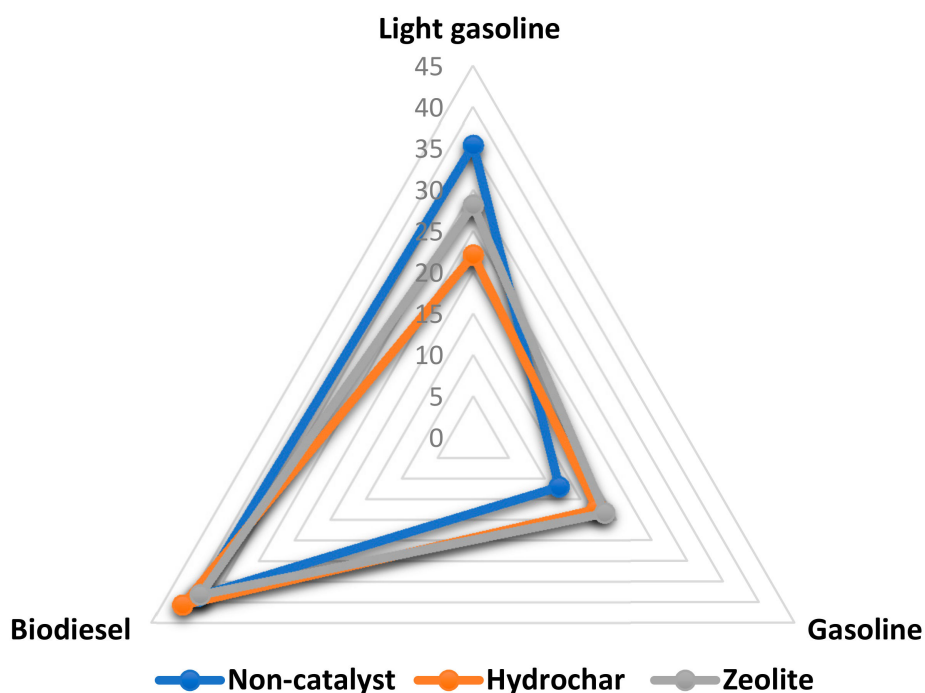


Figure 4. Comparison of selected petroleum products in terms of selectivity (%).

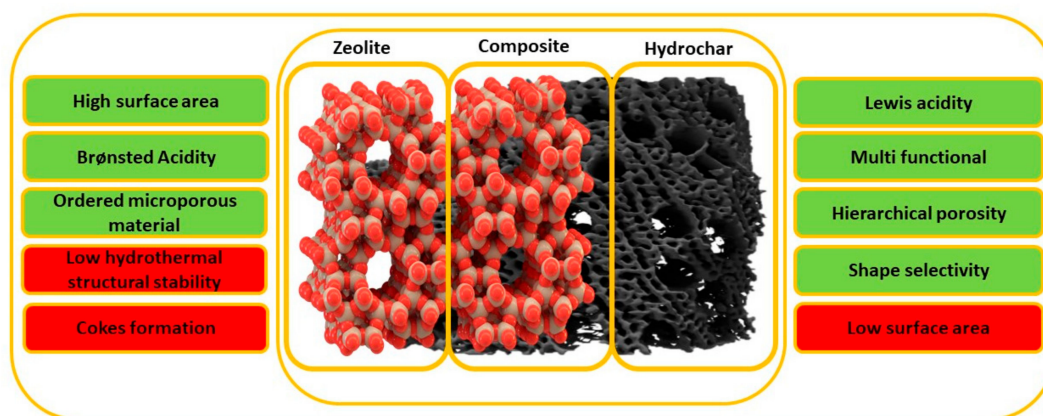


Figure 5. Advantages and disadvantages of zeolite and hydrochar catalysts.

3.5. BET Analysis

Table 3 presents the morphological characteristics of hydrochar and zeolite. In terms of pore size distribution, zeolite had pore diameters of less than 2 nm, which is an indication of its narrow pore size distribution. However, the pore size of hydrochar is distributed mainly with the region of mesopores (20–30 nm), which makes it a better host for macromolecules [31]. The surface area of hydrochar and zeolite were 10 and 603 m² g^{−1}, respectively. Thus, hydrochar solely, without chemical and/or physical treatments, cannot be used as a catalyst support. Total pore volumes of hydrochar and zeolite were 0.45, and 0.65 cm³/g. Hydrochar had a higher pore volume, which has been inherited from the 3D structure of hydrochar.

Table 3. Surface morphology data.

Morphological Characteristic	Units	Hydrochar	Commercial Zeolite
BET surface area	m ² /g	10	603
Total pore volume	cm ³ /g	0.45	0.646
Micropore volume	cm ³ /g	0.001	0.384
Mesopore volume	cm ³ /g	0.54	0.123
Micropore surface area	m ² /g	0.03	466
Mesopore surface area	m ² /g	9	137
Average pore diameter	Nm	25	1.75

4. Conclusions

The physical and chemical characteristics of the hydrochar derived from fruit wastes may not meet those of the conventional fuels. However, it may be a promising candidate as a sustainable carbon part of composites. This study used CP for the catalytic and noncatalytic hydrothermal liquefaction experiments. The advantages and disadvantages of using hydrochar and zeolite catalysts were thoroughly discussed after characterization by Py-GCMS analysis. In noncatalytic HTL of CP, organic acids (10.15%) and furans (3.7%) are the main components, which are mostly derived from the initial fragmentation of the C6 sugars like fructose and glucose. In catalytic tests, both hydrochar and zeolite not only mitigated the corrosive nature of hydrocrude, but also showed high selectivity for hydrocarbon (16.34%) and phenols (25.19%), respectively. In addition to that, the selectivity of levoglucosan decreased significantly in both catalytic scenarios. The results emphasize the necessity of producing a composite, composed of hydrochar and zeolite. Our hypothesis about the catalytic effect

of hydrochar/zeolite composite relies on the combination of different catalytic effects in hydrochar and zeolite.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1996-1073/13/24/6600/s1>, Table S1: Chemicals identified in the biocrude derived from Cranberry.

Author Contributions: O.N. designed the experiments and performed experimental work; M.H. and A.D. have helped in scientific discussion to revise manuscript; M.M.M. have characterized the feedstock composition; O.N. and M.H. wrote the manuscript; A.D. supervised the group during the entire process of project. All authors have read and agreed to the published version of the manuscript.

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

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