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Artificial Coalification of Orange Peel for Extraction of Value Added Chemicals

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Abstract

Waste to value added products is the aim of circular economy. Typical waste to value processes such as composting, briquetting, digestion are time consuming and gasification, and pyrolysis only produces energy. In the present research, a thermochemical process called as hydrothermal carbonization process is used to convert the organic wet waste to useful products. The HTC process converts the organic wet waste into coal like high carbon content material called hydrochar and the liquid component called as biocrude. The biocrude is a mixture of chemicals such as 5-HMF, Levulinic acid, Furfural and other chemicals used in pharmaceutical and cosmetic industry. Orange peel waste is processed in a HTC reactor in temperatures ranging between 180 to 220ºC, with the autogenous pressure. The calorific value of hydrochar produced is measured using bomb calorimeter, and is found to have enhancement over the feedstock. The biocrude is analysed using UV spectrometer and gas chromatography and mass spectroscopy to identify the components present. Compounds including anti-fungal, and anti-bacterial molecules are identified and reported.

Keywords: *Orange Peel, Hydrothermal carbonization, Brake thermal efficiency, Brake specific fuel consumption.*

1.0 Introduction

There are more than 20 varieties of oranges grown apart from the wild variety from the Rutaceae family. Among those, Citrus sinensis (L.) Osbeck (CSO) is a fruiting plant found in warm tropics growing throughout the year. The production of the fruit exceeds 6.7×10^7 tonnes per year, with Brazil being the leading producer (De Arruda et al. 2008). One of the important reasons to use CSO oranges in various industrial products are the accessibility of sugar, and juice with minimal of processing (De Arruda et al. 2008). Agro-products such as fresh fruit, juice, marmalade, flavour, fragrance, colour additives, and pectin derived from CSO are well known. It is estimated that 40 to 50% by weight of orange is wasted as seeds and peels (Lei, Kannan, and Raghavan 2021). The byproduct of this processing industry is the orange peel. These peels is a source of macro nutrients such as dietary fibre, pigment, and sugar derivatives. The orange peel further contains micro nutrients essential oils, polyphenols, hydroxy acids, coumarins, catechins, pectins, enzymes and additionally, orange peels from CSO peeling process can be attractive to be re-used (Lachos-Perez et al. 2021). The flavonones and sugars found in CSO peels have a variety of applications including artificial flavors, and sweeteners.

The direct usage of dry CSO orange peel hydrochar as combustion fuel requires further processing of CSO orange peels (Ma, Fakudze, and Chen 2021). The orange peels are used for ecological and bioremediation applications including oil spill absorbent for disaster management, (El Gheriany et al. 2020) absorption of heavy metals with the use of activated

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carbon from orange peels (Moreno-Piraján and Giraldo 2012). The value added products are reported including biological active compounds (Mantzouridou, Paraskevopoulou, and Lalou 2015) bio-fertilizer, biogas (Calabro and Panzera 2017) and biological fuel cells (Miran et al. 2016). The Methods to functionalize cotton fabric has been developed based on extraction of non-metals using CSO peel waste (Zayed et al. 2022). Synthesis of silver, and zinc oxide nanoparticles are used in the functionalization of cotton fabric, to provide antimicrobial, and mosquito repellent properties to the cotton fibres (Zayed et al. 2022). The extraction of cellulose fibres produced from orange peel waste to textile is demonstrated by aqueous solution methods (Sachidhanandham 2020). Inorganic metal oxide nanoparticle based orange peel based carbonaceous materials are proposed as a high performance super capacitors (Sun et al. 2015).

Methods of valorisation of CSO orange peel waste are many including bio-methanization (Calabro and Panzera 2017). hydrothermal carbonization (HTC), (Lei, Kannan, and Raghavan 2021), (Xiao et al. 2018) cellulose extraction, (Hu et al. 2017) vermicomposting and pre composting, (De Medina-Salas et al. 2020), (Ravi et al. 2019). Several reviews are dedicated for the topic that detail the storage, pre-processing steps, and conversion of value added products. Of the above methods, hydrothermal carbonization (HTC) can be effectively used on CSO orange peel waste because of lack of high concentration of lignin compared to other lignocellulosic waste. Additionally, orange peel has higher concentration of sugars and lipids that provide hydrochar and biocrude with highest fixed carbon (Xiao et al. 2020).

2.0 Hydrothermal Carbonization

The HTC process is a thermo-chemical route to convert wet biomass into hydrochar and biocrude by application of heat in sub-critical water. It can be understood as a bio-refining process that uses low temperature saturated steam to extract essential chemicals from the waste that goes into biocrude and the remaining bio-material is termed as hydrochar. The hydrothermal reactions can be broadly categorized into hydrolysis, dehydration, decomposition, and re-polymerization reactions (Nicolae et al. 2020). The complex polymeric compounds such as cellulose, and hemicellulose are hydrolyzed to get simpler compounds such as glucose, hexose and pentose sugars. Further dehydration produces 5 hydroxymethyl furfural (5-HMF) type molecules. These molecules are re-polymerized, aromatized to form hydrothermal carbon. These reaction are temperature driven and typical HTC of waste biomass is conducted in the temperature range of 180 to 250°C.

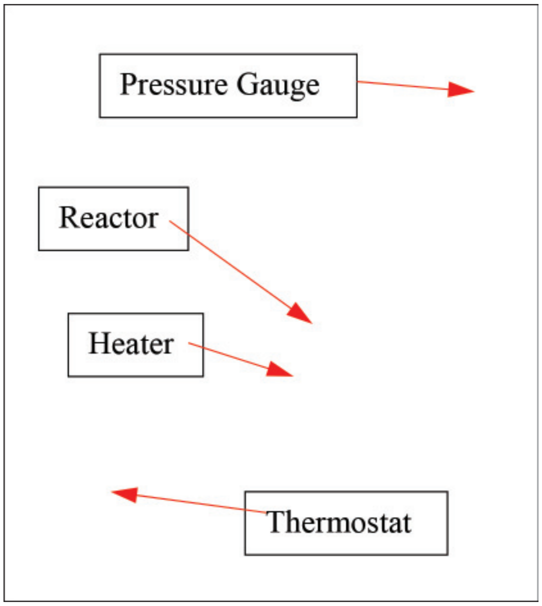

Figure 1: Imageof HT Creactor with temperature regulation rig

Figure 1 shows a HTC reactor of 300 ml capacity, 450 W heater is used in the set up along with a thermostat. The time taken for the set up to reach the set point temperature is about 20-30 minutes. The residence time is counted beyond this initial time required for the set up to reach the set point temperature. The experiments involved addition of 100 ml distilled water with either 10 or 20 grams of orange peel powder. The orange peels were initially dried and ground, a powder is sieved using a standard size of 100 to get a particle size of 150 microns. The temperature set for all the experiments is 200°C, based on the previous HTC experiments and literature recommendation (Batista et al. 2019). The time of experiment is varied for 1, 2 and 3 hours. The severity factor is calculated using the correlation shown in (1). It was found to be in the range from 4.72 to 5.2.

$$R = \log\left(te^{(T-100)/14.76}\right)$$

Table 1: HTC experimental details

Exp no	Feedstock (g)	Temperature °C	Residence time (mins)
1	10	200	60
2	10	200	120
3	10	200	180
4	20	200	60
5	20	200	120
6	20	200	180

3.0 HTC Experimental Results and Discussion

Figure 2 shows the severity factor for the different residence time, as the temperature of the experiments were kept constant.

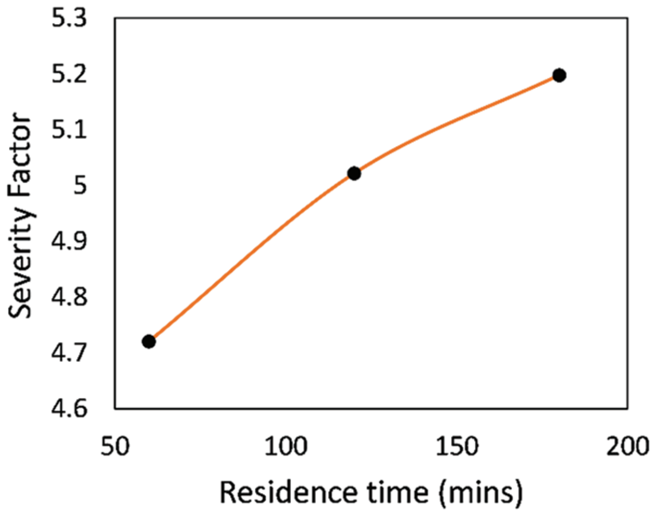

Figure 2: Severity factor vs residence time

Batista et al. 2019 report that the HTC reaction is more sensitive to temperature compared to the residence time. The optimal temperature for the lignocellulosic sugarcane biomass is reported to be about 195ºC (Batista et al. 2019). As the severity factor increases the hydrolysis reaction is enhanced over the condensation and re-polymerization reaction. The hydrochar mass yield reduces and the carbonaceous compounds are found to be present in the biocrude. Figure 3 shows the hydrochar mass yield compared to the residence time. The reduction of hydrochar mass yield with increase in residence time can be due to the dissolution of compounds in hydrochar biomass into the biocrude. The hydrochar yield therefore reduces with increase in residence time and severity factor. The 20% mass ratio experiments have shown similar behaviour as 10% mass ratio. The higher mass ratio during the experimentation leads to the reduction of availability of water in the reactor, and subsequently increased concentration of the organic compounds in the biocrude.

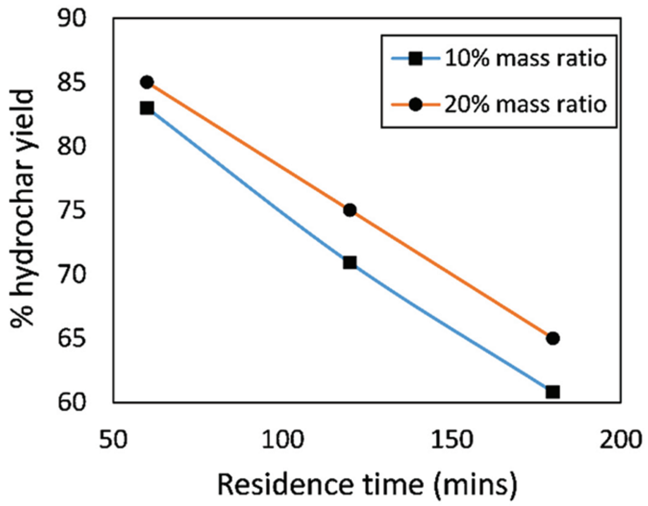

Figure 3: Mass yield vs residence time

Biocrude is the brownish fluid present at the end of HTC reaction. The biocrude obtained from the HTC of orange peels has a distinct flavor of burnt orange peels. The colour and odor of the biocrude is due to the presence of certain compounds. The common types of organic pigment molecules include the â-carotene, punicin, kermesic acid and alizarin type of compounds. The aromatic compounds are typically, the single ring 5 or 6 carbon atom rings, double ringed dienes or its derivatives, and trienes such as anthracenes.

Figure 4 shows the UV absorption spectrum of the biocrude. The absorption wavelength range includes 230 to 330 nm. The inset of the Figure 4 shows the individual peaks in the wavelength range. A simple MatLAB code was developed with the built-in function “findpeaks.m” was developed to identify the peaks in the range. The same method was used to find the peaks for typical biocrude compounds such as Furan, Benzene, Anthracene and Di-Benzo Furan. The UV spectrum of these compounds show peaks in the above range (Nomura, Minami, and Kawamoto 2020). The absorption peaks in the spectrum clearly coincides with peaks of these compounds, and further corroborates the cell wall dissolution as the primary reasons for the presence of these compounds in the biocrude. A number of peaks in the absorption spectrum cannot be correlated to these common molecules. Therefore, absorption spectrum is further analyzed based on the Woodward-Fieser Rule (Hollas, J. Michael. 2004). And an indirect method to infer the presence of the compounds is attempted. From the analysis, it is evident that the peak absorption frequency for single ring structure compounds such as 5 HMF, furan, â-carotene and benzene derivatives is within 300 nm. The peak absorption frequencies for 2-ring structures such as dienes also fall within 320 nm, and the peak absorption for 3 ring structure and its derivatives have higher frequencies.

The peak frequency data confirms the presence of predominantly acyclic and cyclic dienes, with endocyclic double bonds, and exocyclic double bonds.

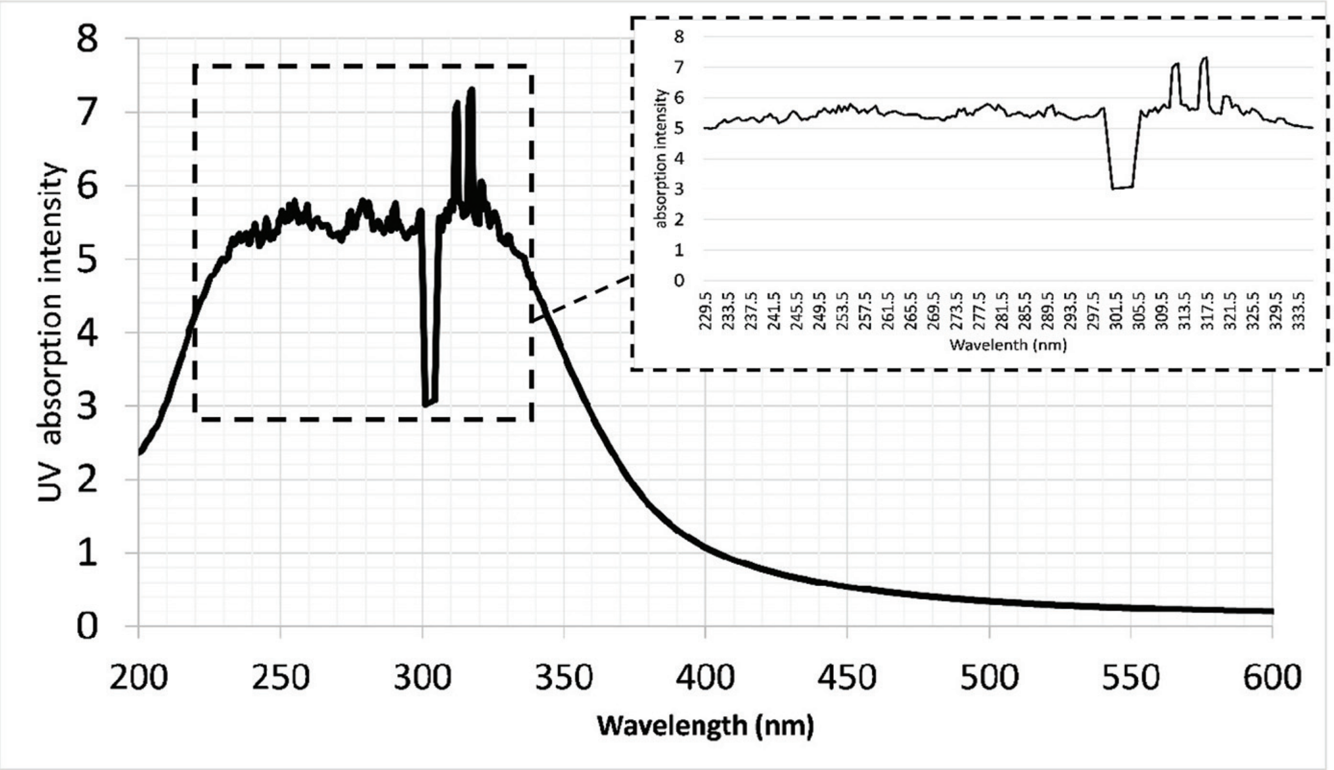

Figure 4: UV spectroscopy absorption spectrum for biocrude from HTC process

3.0 Conclusion

The use of hydrothermal carbonization to process orange peel waste is studied. The process parameters are varied to understand the effects of temperature, residence time and severity factor. UV spectroscopy of the biocrude is conducted and results are analysed using Woodward Fieser Rule. The conclusions from the study is the presence of acyclic and cyclic dienes, benzene derivatives and colour pigments such as â-carotene. Further processing of these compounds from biocrude to isolate with sufficient purity will be part of future work in the project.

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