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Biofuels from Biowaste via a Hybrid Process

Master's thesis in Innovative and sustainable Chemical Engineering

Prabin Dhakal

Department of Chemistry and Chemical engineering

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Supervisor: Abdenour Achour
Examiner: Derek Creaser

Master's Thesis 2022
Department of Chemistry and Chemical engineering
Chemical Engineering Division
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

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Abstract

One of the main challenges the world is facing is global warming caused by greenhouse gas emissions, for which fossil fuels are responsible to a great extent. To combat this issue, there is a need to develop fuels from renewable sources. Food waste can be a potential source of such fuel.

In this study, three different extraction techniques (soxhlet extraction, ultrasound-assisted extraction, and enzyme-assisted extraction) were conducted to characterize Renova's food waste slurry. A new hybrid extraction method has been investigated to enhance the liquefaction, which successfully yielded the highest extracted liquid products. In addition, it investigates catalytic hydrotreatment of the extracted products was evaluated as a food waste valorization strategy to obtain biofuels.

Compared to the three extraction methods, the liquefaction of food waste has been enhanced using the new hybrid extraction method while using ethanol as the solvent in wet conditions. The catalytic hydrotreatment of the extracted liquid and solid obtained from hybrid extraction method produced 87.9 wt% and 74.9 wt% of oil, 7.4 wt% and 13.4 wt% of solids and 7.1 wt% and 14.4 wt% of water respectively, with less than 0.5 wt% gas. Bio-oil from the extracted liquid product consists of 65.5 wt% of alkane-alkenes, 7.6 wt% of cyclic alkanes, 26.5 wt% of alcohol-ether and ketone compounds and less than 1 wt% of aromatics, naphthalenes, and alkylated phenols. Likewise, bio-oil from the extracted solid products consists of 75.6 wt% of alkane-alkenes, 3 wt% of cyclic alkanes, 15.3 wt% of alcohols and ethers 3.3 wt% of aromatics and naphthalenes and 2.8 wt% of alkylated phenols.

Keywords: Biofuels, Bio-oils, food waste, extraction, hybrid extraction.

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1

Introduction

Climate change has been a hot topic of discussion in recent years. The reports and studies show an increase in the global temperature [40]. One of the major contributors is rapid population growth which is inextricably linked to industrialization, transportation, and urbanization. Reliance on fossil fuels has increased in the last decades [3]. Despite tremendous efforts in developing renewable energy from diverse resources, it has only to a contributed relatively small extent. For instance, the US uses 2.9% of the total volume of food waste and disposes of over 35 million metric tons in landfills[2] which causes the food waste to contribute significantly into greenhouse emission. In 2021, 10% of greenhouse gas emissions from food waste has been accounted from the climate change perspective [18].

Food waste contributes significantly to greenhouse gases. The dumping of food waste in landfills or improper disposal leads to the generation of gases like methane and carbon dioxide that directly contribute to climate change. In addition, such food waste treatment methods leads to air pollution, disturbing order, and leachate, directly endangering public health [34]. The typical methods of food waste treatment are incineration, anaerobic digestion, composting, and converting it to animal feed. In addition, researchers have tested other methods including gasification, pyrolysis, hydrothermal liquefaction, and carbonization and supercritical water gasification [34]. However, the dominant methods of food waste treatment in Europe are composting and anaerobic digestion. For example, Sweden uses anaerobic digestion to treat over 60% of food waste [1].

Food waste needs to be used positively towards sustainable energy to remedy climate change and enhance sustainable energy. Thus, biofuels can achieve that, as they are the best alternative for displacing fossil-based fuels. Studies have shown the development of various alternative methods for the production of biofuels. There are multiple feedstocks globally available for this work, such as crops, forestry and agricultural residues, buildings-industrial waste, and municipal solid waste [17].

Food waste is abundant, inexpensive, and has high carbon content. For biofuel production, food waste can be an excellent alternative to lignocellulosic raw materials. The generation of food waste occurs in kitchens, catering, restaurants, food processing plants and industries, and markets. Food waste comprises spoiled food, leftovers, and inedible parts of fruits and vegetables, contributing to one-third of municipal waste [31].

The production of biofuels from food waste as an alternative to fossil-based fuels can solve the environmental threat. In addition, the production of bio-oil creates more value for the end life management of food waste than animal feed or biogas.

Purpose and Aim

This project aims to investigate alternative methods of extraction for valorization of food waste towards production of a deoxygenated bio-oils. To achieve this:

- Various existing conventional and modern extraction methods were studied to finding a suitable extraction method for food waste.
- A Hybrid of conventional and modern methods was investigated to improve the effectiveness for extracted materials.
- Characterization of the extracted materials was carried out using various techniques such as elemental (CHNS-O) analysis, TGA, and gas chromatography.
- Hydroprocessing of extracted compounds was investigated as a process to produce biofuels .
- The liquid and solid products of extraction and bio-oils were analyzed using different characterization method.

2

Literature Study

A literature study was carried out to understand different methods of extraction that can be used in this project which may help to select the extraction technique, and different operating conditions applied. Further, investigation was carried out to understand the nature of feedstocks and existing treatment processes. These findings are explained in this section in more detail.

2.1 Feedstock

Food waste dominates municipal solid waste. The expected population will be 9.5 billion by 2050, which will also increase the food waste. The food wasted through the supply chain is one-third of food produced [34]. Food waste accounts for 8-10% of global greenhouse gas emissions [18]. The annual food waste generation is 931 million tons around the globe, out of which households alone generate 570 million tons of food waste, and the rest comes from retail and foodservices [18]. In the EU, annual food waste is equivalent to 100 million tons and will increase to 120 million tons within five years [5]. Sweden generates 812,948 kg of food waste from households annually [18]. In Sweden, annual food waste generation is 69kg per person from households. Likewise, a yearly food waste generation is 7 kg per person from restaurants, 7 kg per person from catering, and 10 kg per person from retail [11].

The figure 2.1 shows the composition of food waste adopted from anaerobic co-digestion with food waste and wastewater sludge [38]. The food waste includes most fruits, vegetables and starches which is composed of carbohydrates, proteins, lipids, and traces of organic compounds. The composition of food waste varies according to its constituents. For instance, food waste containing rice and vegetables is rich in carbohydrates. Likewise, food waste, including meat and animal-derived products, is rich in proteins and lipids [31].

Table 2.1 presents proximate and ultimate analysis of various food waste, i.e., mixed household food waste and mixed waste from the a food market [8, 29], pomegranate peels, pineapple peels, watermelon peels, garlic peels, green pea, pigeon pea [32], potato peels [24], banana peels, orange peels, citrus peels, lemon peels, and jack fruit peels [33]. Literature reported a carbon-to-oxygen ratio of 1.18 in mixed food waste. In contrast, the moisture of mixed food waste was also higher. Similarly, it comprised the percentage of hydrogen slightly higher than other food waste [8].

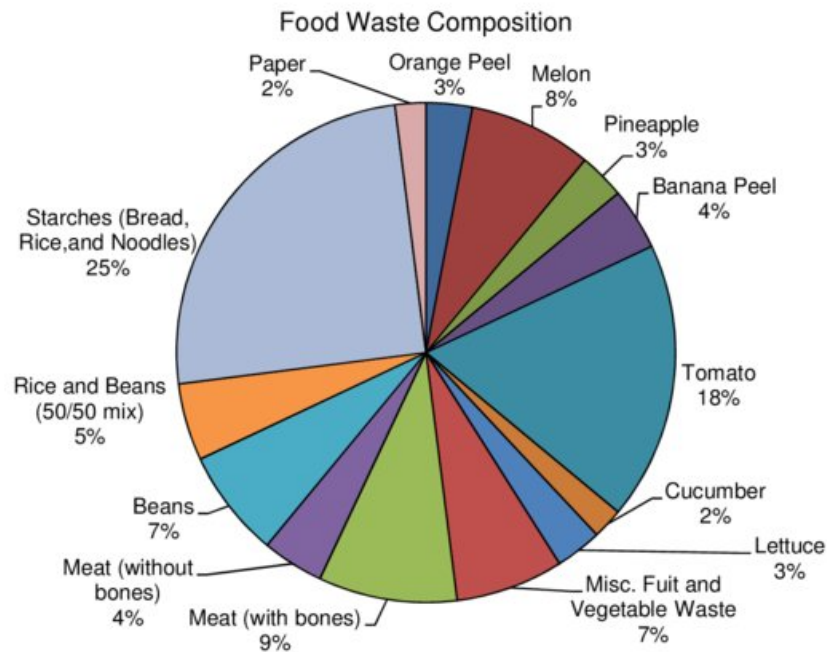


Figure 2.1: Composition of food waste by wet mass, adopted from anaerobic co-digestion of microalgae with food waste and wastewater sludge [38]

2.2 Treatment and Recycling Methods

Some treatment methods use food waste as animal feed or compost it for nutrient recycling [34]. Compositing only works on recycling nutrition and provides no energy recovery. Other methods of food waste treatment are incineration, landfilling, anaerobic digestion, intermediate pyrolysis, fast pyrolysis, hydrothermal liquefaction or gasification, and thermo-catalytic reforming [29].

Disposal of food waste into landfills leads to methane emission, which is more vigorous than carbon dioxide as a greenhouse gas. With energy recovery, food waste incineration reduces volume significantly (80-85%). The heat from the combustion of food waste can run the steam turbine or heat exchangers [34]. But combustion of organics leads to higher carbon emissions [29] and the incombustible ash comprising concentrated inorganic needs to be disposed of properly [34]. In addition, food is not a favorable fuel for incineration as it contains high moisture and non combustible components [34]. Therefore, the EU motivates least on landfilling and incineration of organic waste [30].

Likewise, gasification and pyrolysis seem to be better alternatives to incineration for treating food waste. Pyrolysis converts food waste to bio-oil (17MJ/kg), syngas, and biochar without oxygen. Gasification converts food waste into combustible gas (hydrogen-rich syngas) by partly oxidizing the food at high temperatures(800-900°C). The gas can work as fuel or feed for chemicals production like methanol. Unfortunately, these food waste treatment methods are still under development, and no gasification or pyrolysis appears to be operating only on food waste feed [34].

Thermo-catalytic reforming uses intermediate pyrolysis (450°C) and catalytic re-

Table 2.1: Proximate and Ultimate analysis of different food waste expressed in weight percentage

	Moisture content	Proximate analysis			ultimate analysis					Reference
		Volatile matter	fixed carbon	Ash	C	H	N	S	O	
Food waste	81.5	93	1.5	5.5	46.36	6.98	1.86	N/A	39.3	[8]
Food market waste	80	77.18	5.12	4.16	50.24	7.96	2.92	0.1	34.18	[29]
pineapple peels	8.86	83.77	0.25	3.63	35.96	4.92	0.65	0.09	58.38	[32]
Water melon Peels	8.19	85.36	0.27	6.18	39.69	6.23	2.23	0.33	51.52	
Garlic peels	5.84	84.94	0.75	5.84	34.48	5.7	0.65	0.26	58.91	
Green pea	5.96	89.2	0.6	5.96	37.7	6.19	1.9	0.14	54.07	
Pigeon pea	5.53	90.7	1.83	5.53	40.9	6.13	1.23	0.14	51.6	
Potato peels		76.5	14.2	9.3	43.8	6	4.1	N/A	42.6	[24]
Banana peels	9.8	85.26	0.07	5.01	40.01	6.14	1.3	0.098	52.22	[33]
Orange peels	7.91	86.7	0.14	5.25	38.91	6.19	1.15	0.11	53.64	
Citrus peels	7.58	86.54	1.56	4.32	38.51	6.2	0.64	0.1	54.55	
Lemon peels	6.1	87.16	1.34	5.4	40.33	5.96	1.27	0.19	52.25	
Jackfruit peels	6.48	86.28	0.92	6.32	40.04	5.86	0.9	0.12	53.08	

forming (700°C) to produce bio-oil (37 MJ/kg), gas-rich in methane and lean hydrogen, and biochar (24 MJ/kg) from food waste. The liquid yield was 25 wt% consisting of 7 wt% oil, 18 wt% aqueous phase, the rest was 53 wt % gas and 22 wt% char. However, the nitrogen content was high, which promoted NO_x emission [29].

Hydrothermal carbonization is a method of food waste treatment that uses wet feedstock. The wet feedstock undergoes different reactions like hydrolysis, condensation, dehydration and decarboxylation to produce hydrochar. Hydrochar is a highly carbonized and energy-densified product. Literature reported the product containing carbon of less than 78.6 wt% from food waste generated from restaurants. The energy content in the hydrochar lies between 15-30 KJ/kg of dry solid. However, finding the application of hydrochar for energy is still a challenge [34]. The hydrothermal liquefaction of food waste in the presence of a CeZrOx catalyst produced oil with over 40% carbon yield and less than 5% gas yield at 300 °C [27]. The widely used process of food waste treatment is anaerobic digestion (AD), where

food waste digestion takes place anaerobically to produce biogas. The biogas comprises methane, carbon dioxide, and traces of other gases like nitrogen, oxygen, and sulfur dioxide. It also produces nutrition-rich digestates, which can work as soil conditioner. However, the main problem with this process is the long duration of microbial activity (20-40 days) and the generation of free ammonia from proteins present in the food. In addition, cations from salts also inhibit the gas yield from AD [34].

Ethanol fermentation is another biological treatment of food waste to produce ethanol as the end product. The treatment approach differs from that of AD in terms of feedstock pretreatment. Alkali, acid or enzymatic pretreatment increases cellulose availability for digestion. The fermentation produces ethanol equivalent to 8.3 to 11.6 KJ per kilogram of total solid from food waste. But the type of pretreatment, usually harsh conditions, degrades sugars, leading to furfural formation, which inhibits the fermentation process [34].

2.3 Sustainability of Extraction Processes

Extraction is a separation technique that separates the desired product from the raw materials. The separation in the extraction process occurs through the following steps : (1) the solvent penetrates the solid matrix; (2) solvent dissolves the solute; (3) solvent diffuses out of the matrix; and (4) collection of extracted solute. Different methods of extraction include solvent extraction, distillation, pressing and sublimation. The Most widely used method is solvent extraction [45]. The conventional solvent extraction methods are maceration, percolation, and soxhlet extraction. Literature reported the soxhlet as being best because it consumes less solvent and time. A cellulose bag, a thimble, holds the sample inside the chamber connected to the collecting flask at the bottom and the reflux condenser at the top. While heating the solvent in the collecting flask to a specific temperature, its vapor condenses, continuous reflux occurs, and extraction becomes a continuous process [6]. Phenolics like pinosylvin were extracted from pine knots using the soxhlet extraction method with acetone-water, ethanol-water, cyclohexane, and hexane at 90°C for approximately 8 hours. The yield of pinosylvin was 36.3%, with aqueous ethanol containing 25% water being the most effective solvent [16]. However, certain claims are that heating near the boiling point might destroy some polyphenols [6]. Nowadays, regarding economic principles, the use of alternative and innovative extraction methods such as microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), pressurized fluid extraction (PFE), and enzyme-assisted extraction (EAE) has increased. These methods are called modern or advanced methods of extraction [6].

Microwave-assisted extraction (MAE) uses energy as microwaves to heat the solvent-sample slurry. Because of heating, the diffusivity increases, and extraction takes place. Further, microwaves also disturb the hydrogen bond because of molecules' dipole rotation, allowing the solvent to penetrate further [6]. Microwave-assisted extraction maximized banana peel phenolics extraction using water as solvent. The gallic acid and catechin are generally used as standard to represent phenolics. The maximum phenolics was 50.55 mg of gallic acid equivalent per g of dry solid with

50 ml solvent per gram of dry solids. [42]. However, the penetration depth is one of the most critical factors affecting microwave processes' scale-up [36].

Pressurized liquid extraction (PLE), also known as accelerated solvent extraction, is an advanced method that combines high pressure with high temperature to improve the solubility and desorption of compounds into the solvent from the plant matrix [6]. High-pressure homogenization extracted phenolics from lettuce waste with a hydro-alcoholic solution of 500 and 750ml/l ethanol concentration with the 50ml solvent per gram of lettuce waste and pressure of 50 and 100 MPa. The results showed that higher pressure led to the decompartmentalisation of oxidative enzymes trapped inside the plant matrix, which after release, no longer separates polyphenol oxidase and that leads to the reduction of phenolics in the extract [35].

Ultrasound-assisted extraction(UAE) relies on the implosion of micro-bubbles created due to ultrasound, which causes rapid tissue disruption, leading to the release of components into the solvent[6]. Ultrasound-assisted extraction from broccoli [44], lettuce waste [35], and pine seeds [25] suggest that UAE is a promising method of extraction. Ultrasound applied for a short time in lettuce waste resulted in a significant increase in the yield of phenolics. Similarly, ultrasound-assisted extraction was more effective for pine seeds than microwave-assisted extraction and pressurized liquid extraction at the same temperature [25]. The total flavonoids (79.7mg catechin equivalent/g extract) reported from star-fruits with methanolic extract increased significantly within 30 minutes of sonication, which decreased when the sonication period was 45 and 60 minutes at room temperature with 10 ml solvent per gram of dry solid [9].

Enzymes assisted extraction (EAE) is an advanced technique that exploits the cell wall degrading the capacity of the enzymes, leading to the weakening of the cell wall and increasing the exposure of the cellular component to the solvent [6]. Different enzymes performed extraction from tomato waste [14], broccoli [44], and agri-food waste [13] and showed effectiveness in increasing the extraction yield. The combination of cellulase 7.5 mg per g fresh weight, pectinase 10 mg per g fresh weight, and papain 1 mg per g fresh weight reported maximum production of phenolics, equivalent to 1.816 g gallic acid per kg fresh broccoli at a temperature of 50°C [14].

2.4 Catalytic Hydrotreatment

Hydroprocessing is where many catalytic hydrogenation processes occur, which saturate unsaturated hydrocarbons and remove sulfur, nitrogen, oxygen, and metals from petroleum products of the refinery. Hydrotreatment is extensively used to improve the quality of the final product [39]. Recently, catalytic hydrotreating of biofuels, specially bio-oils derived from second-generation feedstock, has received considerable attention. Usually, hydrotreating of pyrolysis oil under mild and severe conditions; using a low temperature of 280°C at 1450 psi resulted in 40-79 wt% of oxygen reduction, while under extreme conditions at 350 °C, 2900 psi gives 90 wt% oxygen reduction. Literature shows, typically, the use of the heterogeneous catalyst for the hydrotreatment of bio-oils. Under such conditions of temperature and the pressure of hydrogen gas in the presence of a heterogeneous catalyst, multiple reactions occur: hydrogenolysis, hydrogenation, hydrodeoxygenation, decarboxylation,

decarbonylation, and hydrocracking [43].

Hydrogenation (HG) is a process that saturates double or triple bonds or aromatics with the addition of hydrogen [26]. This process removes unwanted olefins and diolefins from the refinery stream, which gets polymerized in the product. This process is also used to remove polyaromatics that converts to coke on catalysis. These polyaromatic are converted into hydroaromatic compounds [39].

Hydrogenolysis (HGL) is a process in which cleavage by hydrogen of C-C or C-heteroatom occurs typically in the presence of a catalyst. The common use of this method is upgrading fuels in the petrochemical industries and removing elements like sulfur, nitrogen, and oxygen to improve fuel quality and prevent catalyst poisoning. Hydrodesulfurization (HDS) is removing sulfur, hydrodeoxygenation (HDO) removing oxygen, and hydrodenitrogenation (HDN) is removing nitrogen. However, HDS and HDN may not be necessary since bio-oils derived from lignocellulosic material are low on sulfur and nitrogen content [26].

Hydrodeoxygenation removes oxygen from the oxygenated feedstock. Hydrodeoxygenation is carried out in the presence of a heterogeneous catalyst. HDO of vegetable oil has improved the ignition qualities of fuels. The feedstock like fats in milk, vegetable oil, grease, and animal oils has been HDO treated to obtain better quality fuel [28].

Hydrocracking converts heavy distillate into smaller molecules similar to those present in gasoline and diesel. Different steps in hydroprocessing occur based on the severity of the process. Initially, the process starts with the saturation of olefins (HG), followed by HGL with the removal of nitrogen, sulfur, and oxygen. Then if the process is more severe, the cracking of heavier molecules starts. The process severity depends upon the type of feedstock and the molecules present in it [26].

Hydrotreating catalysts are typically heterogeneous and selected based on catalyst activity. Characteristics of catalyst like catalyst life, selectivity, ease of activation, regeneration, price, etc., play a vital role in the selection of catalyst. The most common catalysts used for hydrotreating are CoMo, NiMo, and NiW, with typical support of alumina, silica-alumina, silica, and zeolites. CoMo catalysts are excellent in HDS but are less active toward HDN and HDO. NiMo catalysts are excellent HDN and HDO catalysts. NiMo is preferred for the hydrotreatment of unsaturated feedstock. NiW catalysts have the highest activity for aromatic hydrogenation, but their cost is high [39].

The catalyst particles and pore system are also important, especially when considering heavier feedstock, as pore diffusion limits the reaction [39]. In NiMo catalysts, Mo is an active metal, and Ni as a promoter. Nickel helps in the adsorption of oxygenated compounds at the active sites of MoS₂ by creating vacancies [10].

3

Materials and Methods

The aim of this section is to explain the strategy and research approach used for this study. It presents the motivation for selected methods and describes the process of extraction and analysis in details.

Figure 3.1 describes the steps developed in this research project. This can be done in two steps:

1. Using a qualitative research approach to understand the complexity of food waste extraction clearly, and thereafter quantitative strategy approach to determine the various compounds found into the food waste.
2. Strategically using the extraction method found to be optimal for further catalytical hydrotreatment.

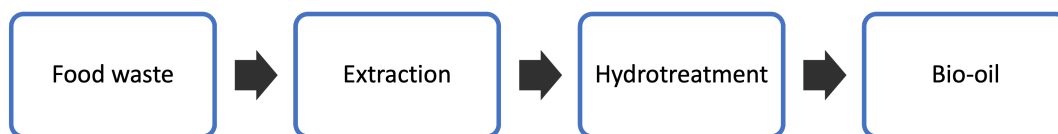


Figure 3.1: Steps for production of biofuels from biowaste, i.e., food waste

3.1 Chemicals and Materials

All of the following chemicals and materials were of analytical grade and were used with no further treatment.

Absolute ethanol, $\geq 100\%$, VWR chemicals(CAS:64-17-5).

Cyclohexane, $\geq 99\%$, Sigma Aldrich(CAS:110-82-7)

Pectinase from *Aspergillus aculeatus*, endopolygalacturonase activity ≥ 3800 units/ml, Sigma Aldrich.

Nickel(II) nitrate hexahydrate, $\geq 99.99\%$, Alfa Aesar, (CAS:13478-00-7).

Ammonium Molybdate tetrahydrate, 99.98%, Sigma Aldrich, (CAS:12054-85-2).

Alumina Spheres, 1.8/210, Sasol Germany.

Extraction Thimble, 501 (cellulose), VWR International bvba, VWR European Cat No. 516-0254

3.2 Preparation of Feedstock Samples

Figure 3.2 shows the food waste received from Renova AB. Food waste was already in the slurry state. Therefore, Renova has pulverized, compressed, strained, and mixed food waste with liquid food waste and prepared it for anaerobic digestion. The slurry was collected from the facility at Marieholm in Gothenburg [4]. This slurry was kept in an air-tight container inside the refrigerator at 5°C and used whenever necessary. The sample of this slurry was dried in an oven for 48 h at 90° for extraction in a dry state.



Figure 3.2: Food waste sample from Renova AB, Gothenburg

3.3 Moisture Determination

As the food waste was in a slurry state, it was necessary to dry it to determine its total solid. A gravimetric method was used to determine the moisture. A sub-sample of raw material was oven-dried for 48 h at 90° and then cooled in a desiccator

for 2 hours to obtain a constant weight. The sub-sample was weighed prior to and after drying. Experiments were done in triplicates with similar results.

3.4 Strategy for Extraction from Food Waste Samples- An Experimental Approach

Three different methods, namely soxhlet, ultrasound-assisted, and enzyme-assisted extraction, and their combination were used. The technique for each will be discussed here in detail in the following sections:

3.4.1 Soxhlet Extraction Method

Soxhlet extraction was performed using the a soxhlet apparatus with a capacity of 250 ml. The three different solvents with different polarity, absolute ethanol, an ethanol-water (1:1 by volume) mixture, and cyclohexane, were used to study the solvent effect on extraction of food waste. Ethanol and water were mixed due to their combined tendency of moderate boiling point, polarity and dielectric constant. Wet solid equivalent to 5 g (22.7 g of wet solid) of dry solid (wet condition) was loaded in a thimble. The ratio of 20 ml solvent to 1 g dried sampled was used. Each experiment was performed for approximately 7 h at 85°C and 95°C.

To further understand the effect of moisture on the extraction process, the extraction was conducted using 5 g of dried samples (dry condition) at 95°C. The ratio of 20ml of solvent to 1g of sampled was used. The amount of solid food waste (dry condition) was increased to 10 g while maintaining the solvent volume to study the equilibrium and saturation rate as a function of sample weight.

3.4.2 Ultrasound-assisted Extraction method

An ultrasound was conducted to generate rapid movement and penetration of solvent using ultrasound at a frequency of 40 kHz and a power of 185 W (Branson,United States). Wet solid equivalent to 5 grams of dry solid (wet condition) was kept inside the reagent bottle of 250 ml. The ratio of 20 ml of solvent to 1 g of sampled was used. The reagent bottle was placed in the water bath for 30 min before starting the sonication allowing the sample's temperature to reach equilibrium with the water-bath's temperature. The temperature effect was conducted at 50°C and 55°C to compare the extraction efficiency and maximize the mass transfer and acceleration of extraction as a function of time (15 and 30 min). The slurry was separated by centrifuging for 6 minutes at 3000 RPM.

3.4.3 Enzyme-assisted Extraction Method

Enzyme-assisted extraction was performed to degrade cell walls and facilitate the extraction. Pectinase (endopolygalacturonase activity ≥ 3800 units/ml) was added to the wet solid, equivalent to 5 g of dry solid (wet condition) and solvent in the 250ml reagent bottle. The resulting efficient solvent from soxhlet and ultrasound

extraction methods was used to carry out the enzymatic assisted extraction method. The ratio of 20 ml of solvent to 1 g of sample was used. 0.26 ml of enzyme per gram of dry solid was loaded, making endopolygalacturonase activity of 1000 units per gram of dry solid. Then the reagent bottle was incubated in an incubator water bath (18L Shaking bath- VWR,US) maintained at 50°C, and shaking of 70 strokes per min was applied for 2 h. The same experiment was repeated using ultrasound bath instead of the incubator. The ultrasound was applied for a predetermined time. The enzymes were deactivated at 90°C for 10 min. The slurry was separated by centrifuging for 6 minutes at 3000 RPM.

3.4.4 Hybrid Extraction Method

The above conventional and modern techniques were conducted to determine their advantages and effective extraction under the used solvents and operating conditions. Their advantageous operating conditions can give maximum yields. These extraction methods were thereby combined to form a new separation technique called a hybrid extraction method.

The hybrid extraction method combined conventional and modern extraction methods. The enzyme solution was incubated with food waste and solvent at 55°C for 2 h and an ultrasound irradiation power was applied. After 2 h the mixed slurry was separated by filtration. A semi-continuous solvent extraction was then carried out using soxhlet method. The obtained solid content has been transferred into a thimble (extraction chamber) and the remaining extracted liquid was placed inside the collecting flask of the soxhlet apparatus. The soxhlet extraction was done for 7 h at 95°C. The deactivation of enzymes and extraction was simultaneously achieved in the soxhlet extraction.

3.5 Solvent Removal from Collected Liquid

The liquid obtained from extraction was filtered under vacuum using a standard crucible filter to obtain the extract free from particles. All the liquid samples were stored in a plastic container with an air-tight lid until further processing. The extract (liquid) was then concentrated using a rotary evaporator (RV8-IKA, Germany) at 50°C. This concentrated liquid is called the extracted liquid product. The weight of liquid product was taken to determine the yield of each experiment. The liquid product was then collected in a 20ml glass vial and stored for further analysis. The solid residue obtained from the extraction was dried in the oven at 90°C overnight, weighed, and stored in an air-tight container for further analysis. This dried residue of solid is referred to as the extracted solid product.

3.6 Hydroprocessing of extracted products

3.6.1 Synthesis of Catalyst

The catalyst was prepared by an incipient wetness impregnation route. Firstly, the γ -alumina support was calcinated at 450°C for 4.5 h in air. Next, the calcinated alumina pellets were crushed and sieved to a size fraction $\geq 250 \mu\text{m}$. Nickle (II) nitrate hexahydrate and ammonium molybdate tetrahydrate were dissolved in absolute ethanol at 50°C with stirring. The crushed support was added slowly with continuous stirring. After 2 hours of stirring, the temperature was increased to 80°C to evaporated ethanol. The paste obtained was dried at 110 °C for 12 hours. The dried catalyst was calcined at 450 °C for 4.5 hours.

3.6.2 Catalytic Hydrotreatment Studies

The hydroconversion of liquid and solid extracted product from Renova's Food waste extraction was performed in a 450ml autoclave batch reactor (Parr Instruments company, US) . The extracted products from the novel hybrid extraction were selected due to the optimized extraction product. The solid product was ground and sieved to a fraction size $\geq 100\mu\text{m}$. Typically, the ratio of catalyst to feedstock was 1:5 by weight and dissolved in 55 g of Hexadecane. After closing the reactor and leak controlling, the mixture was pressurized and heated to the intended temperature while stirring. Once the hydrotreatment was completed, a gas sample was collected at room temperature for further analysis and solids and liquid products were separated using a standard glass crucible filter. The liquid product obtained after rinsing solids with acetone was separated into oil and water using separating funnel after evaporation of acetone. Finally, the solids obtained were treated with dimethyl sulfoxide (DMSO) to determine the conversion. Hydrotreatment was performed by Abdenour Achour.

3.7 Feedstock and Products Analysis

Feedstock and extracted products analysis was performed using various methods as discussed in this section.

3.7.1 Thermal Gravimetric Analysis

A Thermal gravimetric analyzer comprises a furnace where heat supply can be programmed, and a high precision balance records the loss of mass of the sample as a function of temperature [20]. TGA was performed to determine volatile carbon, fixed carbon, and ash content [37]. Degradation of different components under thermal stress was also studied using TGA. TGA was performed in a TGA/DSC 3+ Star system (Mettler Toledo, US) . The sample was dynamically heated from 25 to 900°C at a rate of 10°C/ min. The samples were analyzed under air and nitrogen at a flow rate of 60ml/min.

3.7.2 Elemental Analysis

The elemental composition of a sample is determined using elemental analysis in the form of primary elements, namely carbon(C), hydrogen(H), nitrogen(N), and sulfur(S). Oxygen(O) can be calculated by difference. The result of elemental analysis is needed to determine the quality of fuel by knowing the oxygen content. Furthermore, data can be used to estimate the high heating values.

The elemental analysis (ultimate analysis) was performed in an Elementar vario MICRO cube (Elementar, Germany) calibrated with a sulfanilamide standard.

3.7.3 Gas Chromatography

GC× GC or 2D GC allows superior compound separation in the matrix, which can identify compounds with better resolution [21]. The immense power of separation is achieved by using two columns which are usually coated with different stationary phases [7].

Composition of products in monomeric form was investigated by gas chromatography. Gas chromatography was performed in an Agilent 5977 MSD (Agilent Technologies, USA) where helium was used as carrier gas. The extracted liquid product was diluted with methanol. Compounds were identified by a library search (NIST libraries). The instrumentation and conditions are listed in table 3.1. The calibration and data analysis were performed by Abdenour Achour.

Table 3.1: Instrumentation and condition for GC system

GC-MS	
Gas Chromatograph	Agilent 5977 MSD
1 st Column	VF-1701MS:30m×250μm×0.25μm
	DB-5MS
2 nd Column	DB-5MS:2.6m×150μm×0μm
Oven temperature	25°C-280°C : 3°C/min
Injector Volume	1μl
Column Flow	0.8ml/min
Pressure	12.619 psi
Inlet	280°C, Split ratio 50:1
Split flow	30 ml/min

3.7.4 Karl Fisher

Karl Fisher titration (KF) determines water in samples. KF was used to determine the water in bio-oil samples. Water is determined by a chemical reaction between water present in the sample, alcohol, a base, sulfur dioxide, and iodine [41].

Analysis was performed in 870 KF Titrino plus (Metrohm, US) which was calibrated with a Hydranal water standard.

4

Results and Discussion

4.1 Feedstock Characterization

Prior to the extraction of the food waste slurries, it was essential to characterize the raw materials, for various parameters such as moisture content, TGA and elemental (CHNS-O) analysis.

Table 4.1 shows the moisture content in the food waste slurry. The average Moisture in the food waste slurry was 78 wt%. This result is comparable with those reported in table 2.1.

Table 4.1: Moisture determination for Food waste

Initial weight (g)	Final Weight (g)	Moisture (%)
20.125	4.451	77.883
20.133	4.448	77.907
20.084	4.361	78.286
Average moisture (%) = 78.025		
Standard Deviation = 0.002		

Figure 4.1 illustrates different regions of loss of mass of the dried food waste in an inert atmosphere. The mass loss occurs at a maximum rate of 0.5wt%/°C at a temperature of 285°C due to the decomposition of hemicellulose and cellulose [29]. They represent a significant (68.3 wt%) mass loss due to the devolatilization of organics in the range of 150-400°C [29]. The food waste consists of 79.02 wt% of volatile carbon, 14.91 wt% of fixed carbon, and 4.95 wt% of ash as shown in table 4.2.

Table 4.2 shows the elemental composition of food waste in weight percentage. These results are consistent with those reported in Appendix 2.1. Food waste has a high amount of carbon and hydrogen, which ultimately results in its high heating value. The food waste resulted in a high heating value of 22.28 MJ/kg, which is comparable to coal (24.47 MJ/kg) [15]. Due to the heterogeneous nature of food waste slurry obtained from Renova and huge variability in food waste composition, the results obtained are highly dependent on the sample size taken for analysis and experiments. Therefore, it must be noted that the results obtained may not fully represent the general food waste.

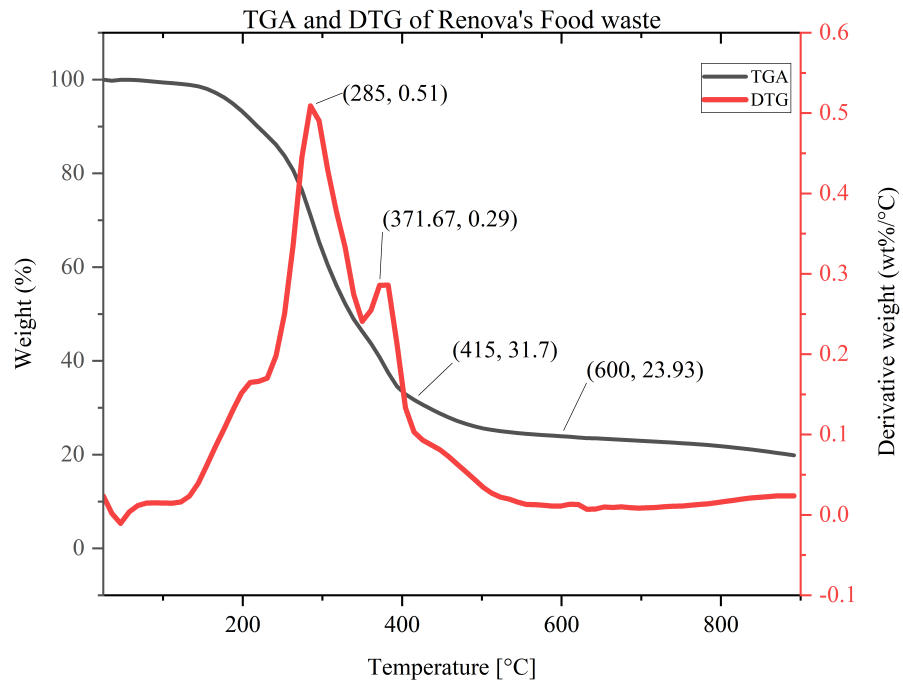


Figure 4.1: TGA and DTG of dried food waste in an inert atmosphere

Table 4.2: Summary of Characteristics of Feedstock

	unit	Value
(Wet solid Basis)		
Moisture	wt%	78.0
(Dry solid basis)		
Volatile carbon	wt%	79.0
Fix Carbon	wt%	1.4
Ash	wt%	4.95
Nitrogen	wt%	3.3
Hydrogen	wt%	8.6
Carbon	wt%	49.4
Sulfur	wt%	0.2
Oxygen	wt%	36.6
HHV	MJ/kg	22.28

4.2 Yield of Extracted Product

This section presents the extraction yield for each process used. The mass balance showed minimum of 96.5 wt% of food waste was converted to liquid and solid products.

Figure 4.2 shows the extracted product yield from the soxhlet extraction method with 5 g of dry solid under wet conditions. Data is provided in Appendix B. At 95 °C, by using ethanol as solvent, the extracted liquid product was 46.4 wt%. At the same temperature, using water-ethanol and cyclohexane as the solvents extracted liquid product was 42.9 wt% and 20.7 wt%, respectively. The low extraction of the liquid products using cyclohexane indicates the presence of lipophilic compounds in small amounts. The use of cyclohexane to extract lipophilic compounds has been reported in star fruits[16]. Figure 4.3 shows the yield of extracted product in a dry state compared with 5 g and 10 g at 95 °C using ethanol as solvent. The extracted liquid product decreased from 46.4 wt% under wet conditions to 30 wt% under dry conditions while using the 5 g of feedstock, indicating the enhancement of extraction of the liquid product due to the presence of moisture. While increasing the amount of feedstock to 10 g in the dry state, it remained almost constant. This suggests the loading rate of solids in the dry state has minimum significance in the extraction of the liquid products.

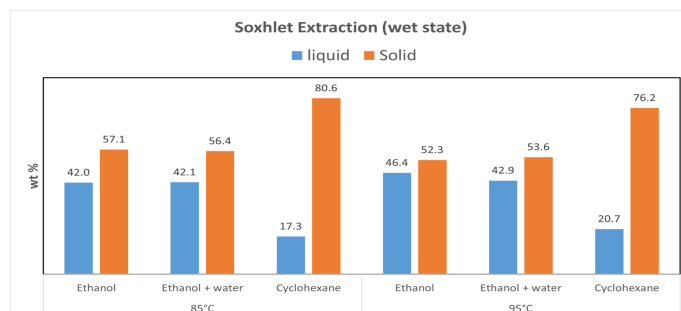


Figure 4.2: Extracted product yield from soxhlet extraction method under wet state at 85°C and 95°C, solvents: ethanol, ethanol-water, and cyclohexane, Solvent to the solid ratio: 20 ml per gram of dry solid and time : 7 h

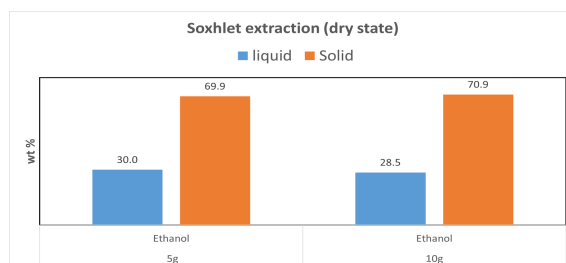


Figure 4.3: Extracted product Yield from soxhlet extraction method dry state at 95°C, solvent: ethanol, Solvent to solid ratio: 20 ml per gram (5 g) and 10 ml per gram (10 g), extraction time : 7 h

4. Results and Discussion

Similarly, figures 4.4 and 4.5 show the extracted product yield using ultrasound-assisted extraction under wet conditions at 50°C and 55°C, respectively. Tables are provided in Appendix B. The figures show that the higher temperature of 55 °C was better for extracting the maximum liquid product. Similar to the results of the soxhlet extraction, ethanol was an effective solvent for extraction at 55°C. 15 min of sonication time yielded the maximum liquid product of 36.1 wt%. The amount of extracted liquid product using ethanol-water and cyclohexane is relatively low. However, the use of cyclohexane resulted in higher yield of liquid products than in soxhlet extraction. This was the effect of the application of the centrifuge, which extracted water present in the form of moisture along with some liquid product in it. The clear phase separation of cyclohexane and water was observed in the collected solvent.

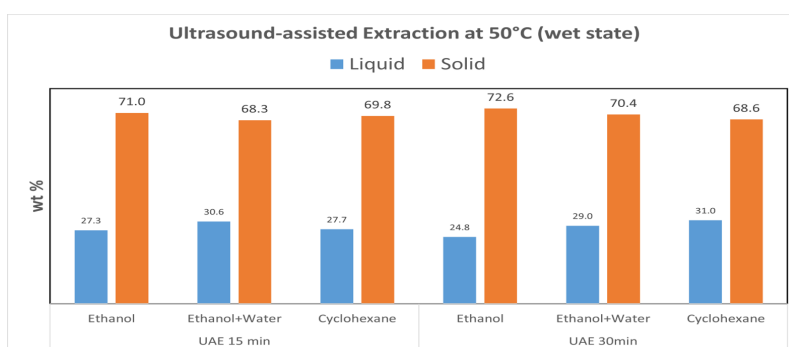


Figure 4.4: Extracted product yield from ultrasound-assisted extraction method in wet condition at 50°C, solvents: ethanol, ethanol-water, and cyclohexane, Solvent to the solid ratio: 20 ml per gram of dry solid and sonication period: 15 and 30 min

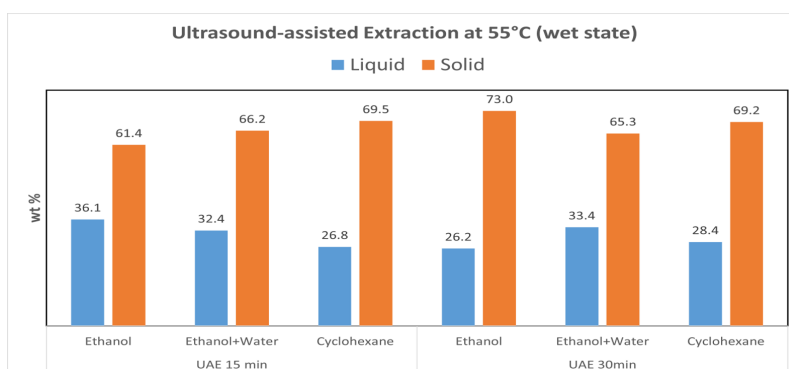


Figure 4.5: Extracted product yield from ultrasound-assisted extraction method in wet condition at 55°C, solvents: ethanol, ethanol-water, and cyclohexane, Solvent to the solid ratio: 20 ml per gram of dry solid and sonication period: 15 and 30 min

Figure 4.6 shows the extracted product yield for enzymatic-assisted extraction using ethanol and ethanol-water as a solvent under wet conditions. The figure compares the use of an incubator and ultrasound bath with ethanol as a solvent. The table is provided in Appendix B. Enzyme-assisted extraction yielded the liquid products in the same range as the ultrasound-assisted extraction using ethanol as solvent. There

was no significant difference between the two solvents: ethanol and ethanol-water. However, comparing the incubation method with the ultrasound method (EAE and UAE combined), the incubator instead of the ultrasound bath enhanced the yield of the liquid product by 5 wt%. This may be due to the better mixing provided by shaking the mechanism of the incubator.

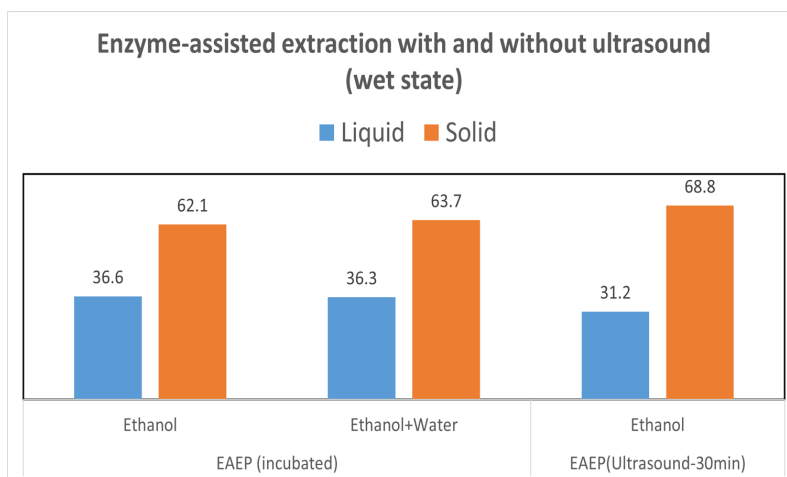


Figure 4.6: Extracted product yield from enzyme-assisted extraction under wet condition using incubator and ultrasound, solvents: ethanol and ethanol-water, Solvent to solid ratio: 20 ml per gram of dry solid and incubation period: 2 h, sonication period: 15 min .

From analyzing of all three extraction methods, we can consider ethanol as a better solvent. Similarly, the higher temperature was favorable (95°C for soxhlet and 55°C for ultrasound). The presence of moisture in the food waste enhanced the extraction of liquid products.

Figure 4.7 shows the result of the hybrid extraction technique under wet conditions using ethanol as solvent. The extracted products from the hybrid method, combining all three extraction methods, enhance the yield of the liquid extracted and reduce solids compared to all three extraction methods. The tables are available in Appendix B. The figure clearly illustrates that extraction of the liquid product increased from 46.4 to 51.5 wt%. This result indicates that the hybrid process can be better for extracting the maximum amount of liquid product than individual extraction methods.

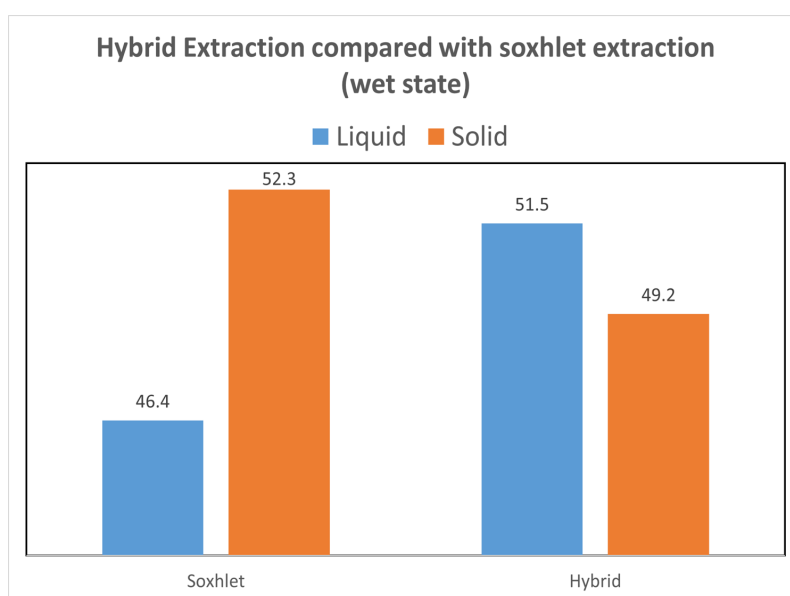


Figure 4.7: Comparison of extracted product yield from hybrid extraction method and soxhlet method extraction at 95°C under wet condition Solvent: ethanol, solvent to the solid ratio: 20 ml per gram of dry solid. Conditions for Hybrid: 2 h incubation at 55° with 15 min sonication and 7 h extraction in soxhlet at 95°C

4.3 Extracted Products Characterization

Characterization in this section shows the analysis on extracted products using soxhlet extraction at 95°C, ultrasound-assisted extraction at 55°C with a sonication period of 15 min, enzyme-assisted extraction using pectinase, and hybrid extraction. Table 4.3 summarizes findings from the TGA and DTG plots of extracted liquid and solid products in an inert atmosphere. Appendix C contains the figures. Maximum degradation of extracted solid products occurs above 300°C for all extraction methods, and the extracted liquid product appears below 285°C, indicating that the solid products contain heavier molecules than liquid. The mass loss of the extracted solid products was less than extracted liquid product for the hybrid extraction process throughout the temperature range. Similarly, the mass lost from the extracted liquid product of the hybrid extraction method was 75.6 wt% at 400°, which was the maximum among all other extraction methods, suggesting the presence of the highest fraction of lighter compounds that depolymerize in that temperature range.

Table 4.3: Summary of TGA and DTG of different extraction products of food waste in an inert atmosphere

Extraction Techniques	Product Type	Maximum Degradation rate(wt%/°C)	Maximum Degradation temperature (°C)	Mass Lost at 400 °C (wt%)	Mass Lost at 600°C (wt%)	Mass Lost at 900 °C (wt%)
Soxhlet_E_95	Liquid	0.4	286.5	63.8	83.19	90.3
	Solid	1.2	321.6	70.6	79.7	83.1
UAE_E_15/55	Liquid	0.4	284.5	65.6	79.5	86.5
	Solid	1.	303.9	75.6	6	86.0
EAE_E_50	Liquid	0.6	224.5	67.0	80.5	92.7
	Solid	0.8	303.9	70.6	78.9	81.7
Hybrid_E_55/95	Liquid	0.9	224.3	75.6	84.4	93.0
	Solid	1	321.6	68.8	78.4	81.9

Soxhlet_E_95: Soxhlet using ethanol at 95 °C, UAE_E_15/55: ultrasound-assisted extraction using ethanol at 55°C with 15 minutes sonication, EAE_E_50: Enzyme assisted extraction at 50°C using ethanol as solvent and Hybrid_E_55/95: Hybrid extraction using ethanol at 95°C and 55°C

Table 4.4 shows the elemental (CHNS-O) analysis of extracted liquid and solid products. Solid products contained oxygen in the range of 41 to 22 wt%, whereas extracted liquid products contained oxygen in the range of 35 to 52.6 wt%. Extracted solid and liquid products were composed of similar hydrogen contents except solid from the soxhlet extraction method. Similarly, sulfur content was insignificant in all the extracted products. However, the nitrogen content of extracted solid products was higher than extracted liquid indicating retention of nitrogenous compounds in the solid products during extraction.

The oxygen content in extracted solid products reduced from 41.1 wt% using the soxhlet method to 22.8 wt% using the hybrid method. The oxygen content in the extracted liquid products increased from 38.1 wt% using the soxhlet method to 52.6 wt% using the hybrid method. This suggests the effectiveness of the hybrid method in the extracting large concentrations of oxygenated compounds. Solid products from the hybrid method contained 10.1 wt% hydrogen and 52.4 wt% carbon, which is higher than the raw food waste.

4. Results and Discussion

The table also shows the ash content in the extracted liquid and solid products obtained from the TGA in the air. The ash content of the extracted liquid and solid product was 4.0 wt% and 8.6 wt% ,respectively while using the hybrid extraction method.

Figure 4.8 shows the Van Krevelen diagram of the extracted liquid and solid products. The Van-Krevelen diagram is used to investigate the chemical composition and decomposition of fuels. The figure shows that extracted liquid products had higher O/C and H/C than the extracted solid products. As the hybrid extraction occurs, the extracted solid product becomes more saturated with aromatic and carbonaceous compounds, causing a decrease in O/C and H/C ratios. A decrease in O/C and H/C ratios were reported with an increase in aromatics and carbonaceous compounds in the case of the pyrolysis oil [19].

Table 4.4: Elemental Analysis of extracted products from different extraction techniques and ethanol as solvent

Techniques	Product	N [%]	C [%]	H [%]	S [%]	ASH [%]	O[%]
Sox_95	Liquid	1.7	43.9	10.8	0.3	5.6	38.1
	Solid	2.7	40.1	7.9	0.1	8.1	41.1
UAE_15/55	Liquid	1.7	36.8	10.7	0.1	3.6	47.12
	Solid	2.4	49.6	9.6	0.1	9.1	29.2
EAE_50	Liquid	1.5	33.3	9.9	0.1	3.5	51.7
	Solid	4.6	50.6	9.7	0.2	5.1	29.9
Hybrid_55/95	Liquid	0.5	31.5	9.4	0.0	3.9	52.6
	Solid	5.8	52.4	10.1	0.3	8.6	22.8

Sox_95: Soxhlet at 95 °C, UAE_15/55:ultrasound-assisted extraction at 55°C with 15 minutes sonication, EAE_50: Enzyme assisted extraction at 50°C and Hybrid_55/95: Hybrid extraction at 95°C and 55°C

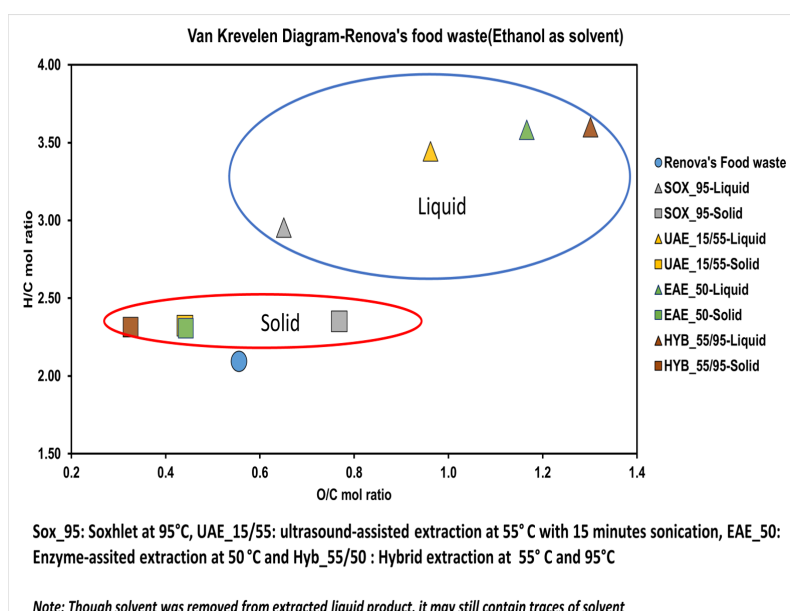
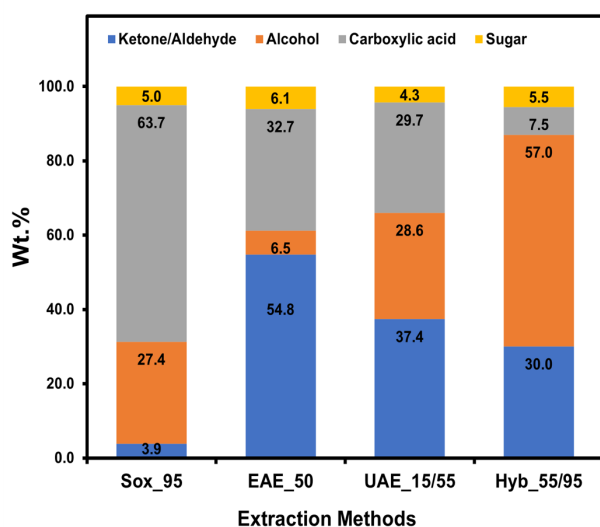


Figure 4.8: Van Krevelen Diagram of the extracted products from food waste using different extraction techniques and ethanol as solvent



Sox_95: Soxhlet at 95°C, UAE_15/55: ultrasound-assisted extraction at 55° C with 15 minutes sonication, EAE_50: Enzyme-assisted extraction at 50° C and Hyb_55/50 : Hybrid extraction at 55° C and 95°C

Figure 4.9: GC× GC identified compounds expressed in weight percentage present in extracted liquid product while using ethanol as solvent

Figure 4.9 shows the identified compounds by GC× GC-MS-FID in the extracted liquid product. Irrespective of the methods, extracted liquid consists of about the same amount of sugar compounds. The carboxylic acid decrease in the order of soxhlet, enzyme-assisted, Ultrasound-assisted, and hybrid. The enzyme-assisted extraction yielded 6.5 wt% of alcohol, whereas the hybrid technique yielded 57.8 wt% alcohol. Carboxylic acid reduced from 63.7 wt% using the soxhlet extraction to 7.5 wt% using hybrid extraction. This might be because of the combined effect of enzymes and ultrasound, as both methods produce relatively low carboxylic acids than the soxhlet methods. The yield of ketone, aldehyde, and alcohol accounts for 87 wt% of compounds in hybrid extracted product. As, the severity of extraction process moves from the the soxhlet to the hybrid extraction method in the same order as shown in the figure, the composition of liquid extracted products becomes dominant with the compounds like alcohols and ketones. However, the table 4.3 shows that the degradation of compounds in liquid extracted products occurred at higher temperatures. Therefore, it must be noted that detection of all the compounds present in the liquid extracted product may not be possible using GC× GC-MS-FID.

4.4 Yield from Hydrotreatment of Extracted Products

The extracted liquid and solid product fraction from the hybrid extraction method were hydroprocessed via a catalytic hydrodeoxygenation reaction at 400°C, 80 bar (H₂), 1000 rpm for 5 h. Figure 4.10 shows the conversion and yield of different products. Conversion of the extracted liquid and solid products were 97.6 wt% and 97.8 wt%, respectively. The oils produced from extracted liquid and solid products were 87.9 wt% and 74.5 wt% (including the oil in both the hexadecane and acetone phases), respectively. The solids from the feed of the liquid and solid extracted products were 7.4 wt% and 13.4 wt%, respectively. The ash content values in table 4.4 were close to this amount of solids. Thus, it may be difficult to lower the solid yield from the hydrotreatment. The acetone phase was separated using the separating funnel to get 7.1 wt% and 14.4 wt% of water, respectively, from the feed of the extracted liquid and solid products. The separated oil from water was analyzed using Karl fisher and the water content in oil was not found. The gas yield was less than 0.5 wt% in both the cases. The oil yield was better than the thermal catalytic cracking process in which pyrolysis gas from food waste was cracked at 700°C. The thermal catalytical cracking reported yield of 7 wt% oil, 18 wt% aqueous phase, 22 wt% char and 53 wt% gas from food waste [29].

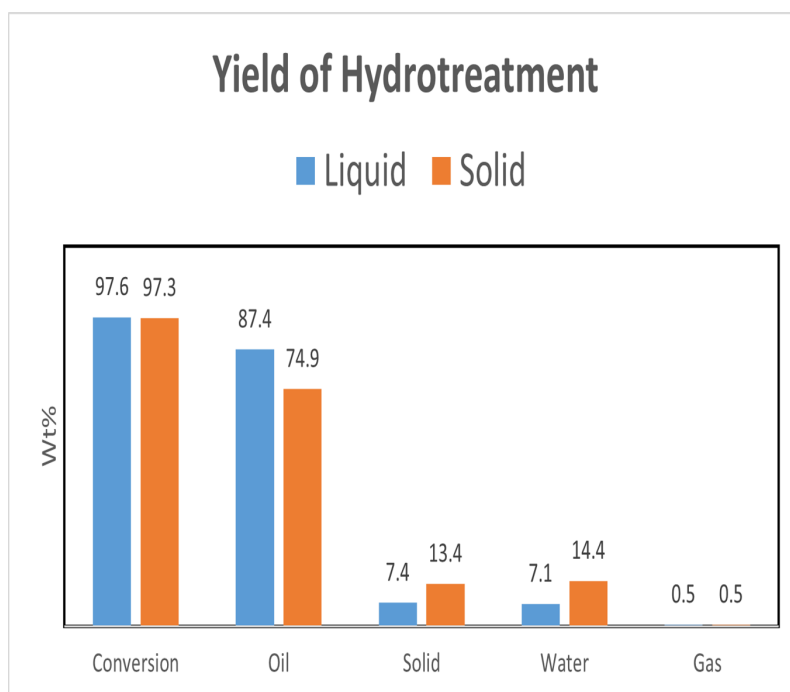


Figure 4.10: Yield of different products from hydrotreatment for solid and liquid extracted products obtained using hybrid extraction method. Catalyst to feed ratio: 1: 5 by weight and 55 g of hexadecane.

4.5 Bio-oil Characterization

This section presents the characterization of the bio-oil resulting from hydroprocessing of the extracted liquid and solid products of food waste using TGA and GC×GC-MS-FID.

Figure 4.11 shows the TGA and DTG curve for the bio-oil obtained from the hydrotreatment of extracted liquid and extracted solid products. The oil from the extracted liquid product loses all mass below 215°C, whereas oil from the extracted solid product loses around 98.6 wt% of its mass at same temperature. TGA diagrams resembles that of the diesel [22]. The maximum mass loss rate peak appears at a difference of 8.8°C between oil from the liquid and solid extracted products indicating the presence of heavier compounds in oil from the solid.

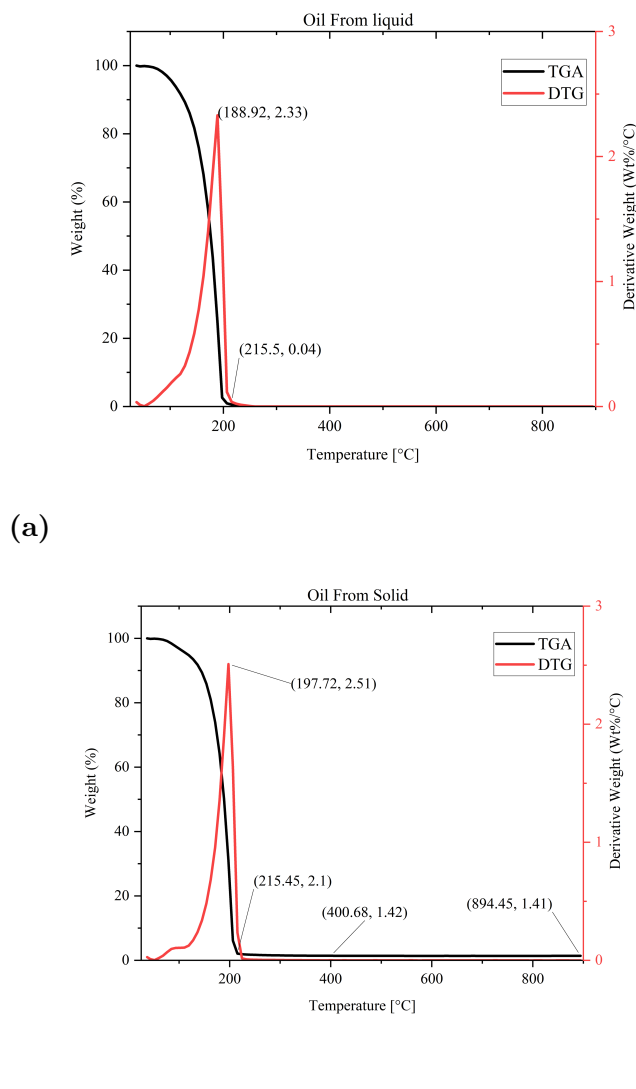


Figure 4.11: TGA and DTG plot of Bio-oil in inert atmosphere from extracted (a) liquid Product and (b) solid Product

Figure 4.12 shows the identified compounds in the product bio-oil using GC× GC-MS-FID data obtained from both extracted liquid and solid products. The solid and liquid product's oil consists of 75 wt% and 65.5 wt% of alkanes-alkenes, respectively. The alcohol-ketone compounds were 26.4 wt% and 15.3 wt% in liquid and solid oils, respectively. The extracted solid product's oil consists of 2.8 wt% and 3.3 wt% of alkylated phenols and aromatics-naphthalene respectively. This class of compounds were present in insignificant amounts in oil from the liquid extracted product. Furthermore, oil from solid extracted had 2.8 wt% of alkylated phenols. The results showed catalytical deoxygenation of most oxygenated compounds to form alkanes and alkenes. There was drastic reduction in presence of alcohol, aldehyde and ketone in the oil from the liquid extracted product. On the other hand, these compounds were dominant in the extracted liquid product from the hybrid extraction method. The aromatics were present in the solid as explained by Van krevelen diagram, which is present in the solid's oil product. Cyclic alkane appears from the deoxygenation of cyclic alcohol, ketone, and aldehyde [23]. The aromatic compounds can also be hydrogenated to form cyclic alkanes. The source of alcohol can be traced back to the alcohol originally present in the feed in the case of the liquid extraction product. Furthermore, analysis is required to understand the presence of other compound such as alcohol, ketone, and alkenes-alkanes in solid's oil. There were large numbers of compounds in the extracted liquid products. Therefore, it must be noted that it may be difficult to fully comprehend the mechanism occurred during the hydrotreatment without further analysis.

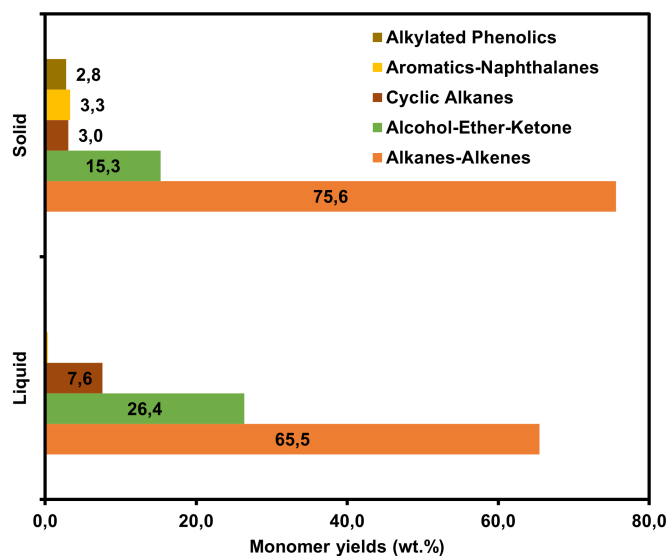


Figure 4.12: GC*GC MS-FID identified monomer compounds in bio-oil yield from hydrotreatment of solid and liquid extracted products

5

Conclusion

The liquefaction of food waste using the hybrid extraction method was an effective method. The extraction can work successfully using ethanol under wet conditions and prevent drying. The maximum liquid product obtained was with a combination of the soxhlet at 95°C and the ultrasound at 55°C with the application of the ultrasound for 15 min and pectinase as the enzyme. The hybrid extraction method yielded 51.5 wt% of food waste as the liquid products. The TGA showed 75.6 wt% and 68.8 wt% of small compounds that get volatilized within in 400°C in the hybrid extracted liquid and solid products respectively. Furthermore, the elemental analysis showed the hybrid extracted liquid products contains 52.6 wt% of oxygen and 31.5 wt% of carbon. The hybrid extracted solid products contain 22.8 wt% of oxygen and 52.4 wt% of carbon. Moreover, the hybrid extracted liquid products consists of 87 wt% of ketone, aldehyde, and alcohols.

The hydrotreatment of hybrid extracted products converted 97 wt% into different product fractions. The hydrotreatment yielded 87.4 wt% and 74.9 wt% of oil from extracted liquid and solid products, respectively. The TGA of the oil showed the presence of slightly larger compounds in the oil obtained from the extracted solid product. The TGA and DTG curve was similar to the diesel for oil from both types of feed. The GC×GC analysis of the oils showed the presence of a high quantity of alkanes and alkenes. The extracted liquid and solid products appeared to be cracked and reformed to light monomeric organic compounds. The oil from the feed of hybrid extracted liquid and solid products contained a high quantity of deoxygenated compounds, among which 65.5 wt% of and 75.6 wt% were alkanes and alkenes. Overall, the experimental results were promising for producing biofuels from food waste.

Future work

The hybrid extraction method can be an effective and sustainable. However, there is a need to optimize each extraction method involved in the hybrid extraction. The study of different solvents and operating conditions can make this more productive. The combination of different enzymes can be applied to increase the liquefaction of food waste to a greater extent. Similarly, to understand the mechanism of extraction methods and their role in extracting different components from food waste, the extracted products can be analyzed using FTIR, NMR, MALDI, etc.

Other properties of bio-oil like, calorific value and viscosity, need to be studied before considering it as an option for transportation fuel. The char and water needs to be studied for their properties to find their application and make the process more sustainable. The use of different catalysts can optimize the hydrotreatment param-

5. Conclusion

ters in the future. Further, each extraction method can be optimized to produce the maximum amount of liquid product. However, it is necessary to understand which type of extracted product suits best for the hydrotreatment.

Bibliography

- [1] Bio-waste in Europe — turning challenges into opportunities — European Environment Agency.
- [2] Food: Material-Specific Data | US EPA.
- [3] Global oil demand 2006-2026 | Statista.
- [4] Our facilities | Renova.
- [5] Refresh – towards less food waste in Europe - IVL Svenska Miljöinstitutet.
- [6] Alfredo Aires. Phenolics in Foods: Extraction, Analysis and Measurements. In *Phenolic Compounds - Natural Sources, Importance and Applications*. InTech, 3 2017.
- [7] Mohammed S. Alam and Roy M. Harrison. Recent advances in the application of 2-dimensional gas chromatography with soft and hard ionisation time-of-flight mass spectrometry in environmental analysis. *Chemical Science*, 7(7):3968–3977, 6 2016.
- [8] B. Amuzu-Sefordzi, J. Huang, and M. Gong. Hydrogen production by supercritical water gasification of food waste using nickel and alkali catalysts. *WIT Transactions on Ecology and the Environment*, 190 VOLUME 1:285–296, 2014.
- [9] H V Annegowda, Rajeev Bhat, Min-Tze Liong, A A Karim, and S M Mansor. Influence of sonication treatments and extraction solvents on the phenolics and antioxidants in star fruits. page 2011.
- [10] Prakhar Arora, Houman Ojagh, Jungwon Woo, Eva Lind Grennfelt, Louise Olsson, and Derek Creaser. Investigating the effect of Fe as a poison for catalytic HDO over sulfided NiMo alumina catalysts. *Applied Catalysis B: Environmental*, 227:240–251, 7 2018.
- [11] Avfall Svergie. Waste management in Sweden | Avfall Sverige, 2020.
- [12] Thomas J. Buckley. Calculation of higher heating values of biomass materials and waste components from elemental analyses. *Resources, Conservation and Recycling*, 5(4):329–341, 1991.
- [13] M. Castrica, R. Rebutti, C. Giromini, M. Tretola, D. Cattaneo, and A. Baldi. Total phenolic content and antioxidant capacity of agri-food waste and by-products. *Italian Journal of Animal Science*, 18(1):336–341, 1 2019.
- [14] Gizem Catalkaya and Derya Kahveci. Optimization of enzyme assisted extraction of lycopene from industrial tomato waste. *Separation and Purification Technology*, 219:55–63, 7 2019.
- [15] T. Cordero, J. Rodríguez-Mirasol, J. Pastrana, and J. J. Rodríguez. Improved solid fuels from co-pyrolysis of a high-sulphur content coal and different lignocellulosic wastes. *Fuel*, 83(11-12):1585–1590, 8 2004.

- [16] Wenwen Fang, Jarl Hemming, Markku Reunanen, Patrik Eklund, Enma Conde Pineiro, Ida Poljansek, Primoz Oven, and Stefan Willför. Evaluation of selective extraction methods for recovery of polyphenols from pine. *Holzforschung*, 67(8):843–851, 12 2013.
- [17] M. Fatih Demirbas, Mustafa Balat, and Havva Balat. Biowastes-to-biofuels. *Energy Conversion and Management*, 52(4):1815–1828, 4 2011.
- [18] Hamish Forbes, Tom Quested, and Clementine O’connor. UNEP Food Waste Index Report 2021 | UNEP - UN Environment Programme, 2021.
- [19] Peng Fu, Weiming Yi, Xueyuan Bai, Zhihe Li, Song Hu, and Jun Xiang. Effect of temperature on gas composition and char structural features of pyrolyzed agricultural residues. *Bioresource Technology*, 102(17):8211–8219, 9 2011.
- [20] Morten Grønli. *Theoretical and experimental study of the thermal degradation of biomass*. PhD thesis, The Norwegian University of Science and Technology, 1996.
- [21] Lisa N Kates, Philip I Richards, and D Sandau. The application of comprehensive two-dimensional gas chromatography to the analysis of wildfire debris for ignitable liquid residue. 2020.
- [22] R. S. Leonardo, M. L. Murta Valle, and J. Dweck. Thermovolumetric and thermogravimetric analysis of diesel S10: Comparison with ASTM D86 standard method. *Journal of Thermal Analysis and Calorimetry*, 139(2):1507–1514, 1 2020.
- [23] Jianbin Li, Chia Yu Huang, and Chao Jun Li. Deoxygenative Functionalizations of Aldehydes, Ketones and Carboxylic Acids. *Angewandte Chemie - International Edition*, 61(10), 3 2022.
- [24] Shaobo Liang, Yinglei Han, Liqing Wei, and Armando G. McDonald. Production and characterization of bio-oil and bio-char from pyrolysis of potato peel wastes. *Biomass Conversion and Biorefinery*, 5(3):237–246, 9 2015.
- [25] Ali Liazid, Monica Schwarz, Rosa M. Varela, Miguel Palma, Dominico A. Guillén, Jamal Brigui, Francisco A. Macías, and Carmelo G. Barroso. Evaluation of various extraction techniques for obtaining bioactive extracts from pine seeds. *Food and Bioproducts Processing*, 88(2-3):247–252, 6 2010.
- [26] Markus Lilja. Catalytic hydrotreating of lignin, 9 2019.
- [27] Alex R. Maag, Alex D. Paulsen, Ted J. Amundsen, Paul E. Yelvington, Geoffrey A. Tompsett, and Michael T. Timko. Catalytic hydrothermal liquefaction of food waste using cezrox. *Energies*, 11(3), 2 2018.
- [28] Masita Mohammad, Thushara Kandaramath Hari, Zahira Yaakob, Yogesh Chandra Sharma, and Kamaruzzaman Sopian. Overview on the production of paraffin based-biofuels via catalytic hydrodeoxygenation. *Renewable and Sustainable Energy Reviews*, 22:121–132, 2013.
- [29] Miloud Ouadi, Muhammad Asif Bashir, Lais Galileu Speranza, Hessam Jahangiri, and Andreas Hornung. Food and Market Waste-A Pathway to Sustainable Fuels and Waste Valorization. *Energy and Fuels*, 33(10):9843–9850, 10 2019.
- [30] Gómez Palacios, ; Ruiz De Apodaca, ; Rebollo, and ; Azcárate. EUROPEAN POLICY ON BIODEGRADABLE WASTE: A MANAGEMENT PERSPECTIVE.

-
- [31] Kunwar Paritosh, Sandeep K. Kushwaha, Monika Yadav, Nidhi Pareek, Aakash Chawade, and Vivekanand Vivekanand. Food Waste to Energy: An Overview of Sustainable Approaches for Food Waste Management and Nutrient Recycling. *BioMed Research International*, 2017, 2017.
- [32] Pranav D. Pathak, Sachin A. Mandavgane, and Bhaskar D. Kulkarni. Characterizing fruit and vegetable peels as bioadsorbents. *Current Science*, 110(11):2114–2123, 2016.
- [33] Pranav D. Pathak, Sachin A. Mandavgane, and Bhaskar D. Kulkarni. Fruit peel waste: Characterization and its potential uses. *Current Science*, 113(3):444–454, 8 2017.
- [34] Thi Phuong Thuy Pham, Rajni Kaushik, Ganesh K. Parshetti, Russell Mahmood, and Rajasekhar Balasubramanian. Food waste-to-energy conversion technologies: Current status and future directions. *Waste Management*, 38(1):399–408, 2015.
- [35] Stella Plazzotta and Lara Manzocco. Effect of ultrasounds and high pressure homogenization on the extraction of antioxidant polyphenols from lettuce waste. *Innovative Food Science and Emerging Technologies*, 50:11–19, 12 2018.
- [36] Peter Prielcel and Jose Antonio Lopez-Sanchez. Advantages and Limitations of Microwave Reactors: From Chemical Synthesis to the Catalytic Valorization of Biobased Chemicals. 2018.
- [37] Md Sumon Reza, Shafi Noor Islam, Shammya Afroze, Muhammad S. Abu Bakar, Juntakan Taweekun, and Abul K. Azad. Data on FTIR, TGA – DTG, DSC of invasive pennisetum purpureum grass. *Data in Brief*, 30, 6 2020.
- [38] Ruth E Spierling. ANAEROBIC CO-DIGESTION OF MICROALGAE WITH FOOD WASTE AND WASTEWATER SLUDGE, 6 2011.
- [39] Henrik Topsøe, Bjerne S. Clausen, and Franklin E. Massoth. *CATALYSIS-Science and Technology*, volume 11. Springer-Verlag, Berlin, first edition, 1996.
- [40] U.S. Global Change Research Program. Climate science special report: Fourth national climate assessment, volume I. *U.S. Global Change Research Program*, 1:470, 2018.
- [41] J. C. Verhoef and E. Barendrecht. Mechanism and reaction rate of the karl fischer titration reaction: Part V. Analytical Implications. *Analytica Chimica Acta*, 94(2):395–403, 12 1977.
- [42] Hang T. Vu, Christopher J. Scarlett, and Quan V. Vuong. Maximising recovery of phenolic compounds and antioxidant properties from banana peel using microwave assisted extraction and water. *Journal of Food Science and Technology*, 56(3):1360–1370, 3 2019.
- [43] Yun Wang, Hongfei Lin, and Ying Zheng. Hydrotreatment of lignocellulosic biomass derived oil using a sulfided NiMo/ γ -Al₂O₃ catalyst. *Catalysis Science & Technology*, 4(1):109–119, 12 2013.
- [44] Hao Wu, Junxiang Zhu, Long Yang, Ran Wang, and Chengrong Wang. Ultrasonic-assisted enzymatic extraction of phenolics from broccoli (*Brassica oleracea* L. var. *italica*) inflorescences and evaluation of antioxidant activity in vitro. *Food Science and Technology International*, 21(4):306–319, 6 2015.

- [45] Qing Wen Zhang, Li Gen Lin, and Wen Cai Ye. Techniques for extraction and isolation of natural products: A comprehensive review. *Chinese Medicine (United Kingdom)*, 13(1):1–26, 4 2018.

A

Appendix 1

TGA of food waste

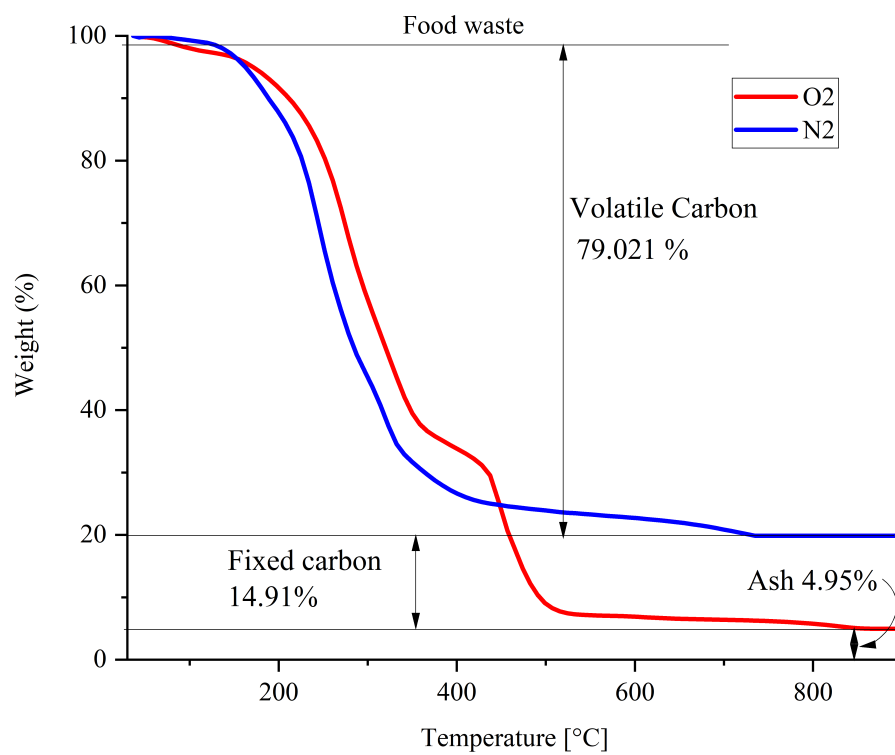


Figure A.1: TGA of food waste slurry using oxygen and Nitrogen

B

Appendix 2

Product yield Soxhlet Extraction

Table B.1: Soxhlet extraction product yield at **85°C in wet condition**

Solvent	Initial Weight (g) [before extraction]	Equivalent Dry Weight(g)	Final Weight (g) [after extraction and drying]	yield (%) [solid-Product]	liquid weight(g)	yield (%) [liquid-product]
Ethanol	22.7	5.0	2.9	57.1	2.1	42.0
Ethanol-Water	22.9	5.0	2.8	56.4	2.1	42.1
Cyclohexane	22.7	5.0	4.0	80.6	0.9	17.3

Table B.2: Soxhlet extraction product yield at **95°C in wet condition**

Solvent	Initial Weight (g) [before extraction]	Equivalent Dry Weight(g)	Final Weight (g) [after extraction and drying]	yield (%) [solid-Product]	liquid weight(g)	yield (%) [liquid-product]
Ethanol	22.7	5.0	2.6	52.3	2.3	46.4
Ethanol-Water	22.8	5.0	2.7	53.6	2.2	42.9
Cyclohexane	22.7	5.0	3.8	76.2	1.0	20.7

Table B.3: Soxhlet extraction product yield **95°C in dry condition** for food waste

Solvent	Initial Weight (g) [before extraction]	Equivalent Dry weight(g)	Final Weight (g) [after extraction and drying]	yield (%) [solid-Product]	liquid weight(g)	yield (%) [liquid-product]
Ethanol	5.5	5.5	3.8	69.9	1.7	30.0
Ethanol	10.0	10.0	7.1	70.9	2.9	28.5
Ethanol-Water	5.0	5.0	2.5	50.6	2.3	46.7
Cyclohexane	5.0	5.0	4.1	81.7	0.9	18.7

Ultrasound-assisted Extraction

Table B.4: UAE product yield at 50°C in wet condition with 15 minutes sonication

Solvent	Initial Weight (g) [before extraction]	Equivalent Dry weight(g)	Final Weight (g) [after extraction and drying]	yield (%) [solid-Product]	liquid weight(g)	yield (%) [liquid-product]
Ethanol	22.8	5.0	3.6	71.0	1.4	27.3
Ethanol-Water	22.8	5.0	3.4	68.3	1.5	30.6
Cyclohexane	22.8	5.0	3.5	69.8	1.4	27.7

Table B.5: UAE product yield at 50°C in wet condition with 30 minutes sonication

Solvent	Initial Weight (g) [before extraction]	Equivalent Dry weight(g)	Final Weight (g) [after extraction and drying]	yield (%) [solid-Product]	liquid weight(g)	yield (%) [liquid-product]
Ethanol	22.8	5.0	3.6	72.6	1.2	24.8
Ethanol-Water	22.7	5.0	3.5	70.4	1.4	29.0
Cyclohexane	22.7	5.0	3.4	68.6	1.5	31.0

Table B.6: UAE product yield at 55°C in wet condition with 15 minutes sonication

Solvent	Initial Weight (g) [before extraction]	Equivalent Dry weight(g)	Final Weight (g) [after extraction and drying]	yield (%) [solid-Product]	liquid weight(g)	yield (%) [liquid-product]
Ethanol	22.7	5.0	3.1	61.4	1.8	36.1
Ethanol-Water	22.8	5.0	3.3	66.2	1.6	32.4
Cyclohexane	22.8	5.0	3.5	69.5	1.3	26.8

Table B.7: UAE product at 55°C in wet condition with 30 minutes sonication

Solvent	Initial Weight (g) [before extraction]	Equivalent Dry weight(g)	Final Weight (g) [after extraction and drying]	yield (%) [solid-Product]	liquid weight(g)	yield (%) [liquid-product]
Ethanol	22.7	5.0	3.6	73.0	1.3	26.2
Ethanol-Water	22.7	5.0	3.3	65.3	1.7	33.4
Cyclohexane	22.8	5.0	3.5	69.2	1.4	28.4

Enzyme-assisted Extraction

Table B.8: EAE product yield at 50°C in wet condition with 2 hours incubation

Solvent	Initial Weight (g) [before extraction]	Equivalent Dry weight(g)	Final Weight (g) [after extraction and drying]	yield (%) [solid-Product]	liquid weight(g)	yield (%) [liquid-product]
Ethanol	22.7	5.0	3.1	62.1	1.8	36.6
Ethanol-Water	22.8	5.0	3.2	63.7	1.8	36.3

Hybrid Extraction

Table B.9: Hybrid extraction product Yield at 55°C in **wet condition** with 2 hours incubation and simultaneous 15 minutes sonication followed by soxhlet at 95°C

Solvent	Initial Weight (g) [before extraction]	Equivalent Dry weight(g)	Final Weight (g) [after extraction and drying]	yield (%) [solid-Product]	liquid weight(g)	yield (%) [liquid-product]
Ethanol	22.7	5.0	2.5	49.2	2.6	51.5

C

Appendix 3

Extracted Product Characterization

TGA and DTG

Soxhlet Extraction at 95°C using ethanol as solvent

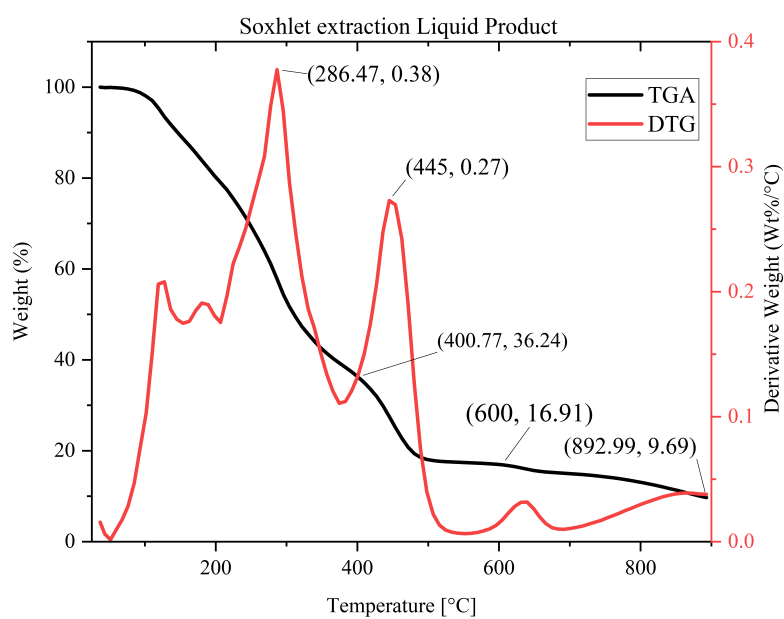


Figure C.1: TGA and DTG of extracted liquid product of Soxhlet Extraction at 95°C

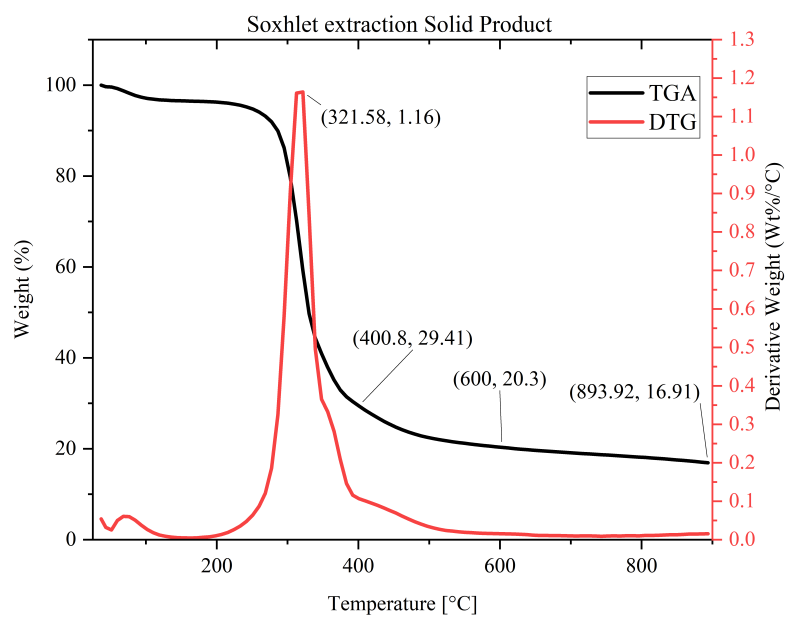


Figure C.2: TGA and DTG of extracted solid product of Soxhlet Extraction at 95°C

Ultrasound-assisted extraction at 55°C and 15 min sonication using ethanol as solvent

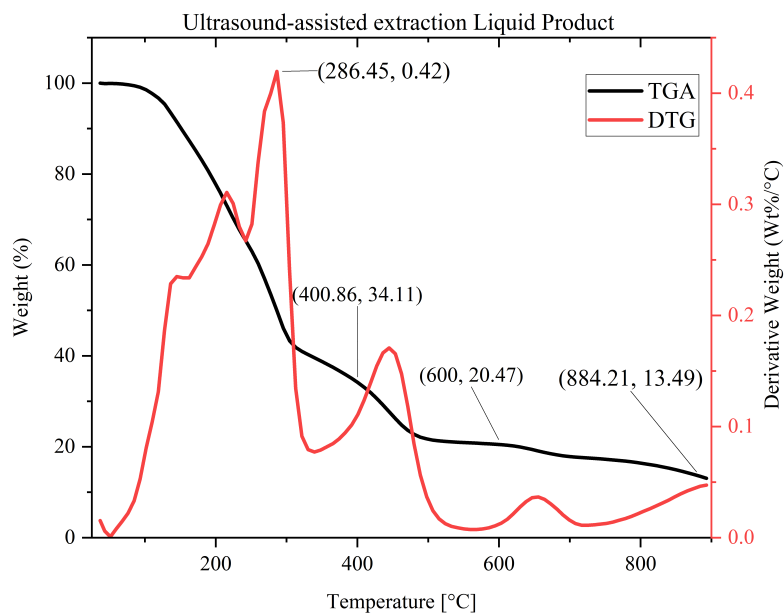


Figure C.3: TGA and DTG of extracted liquid Product of UAE at 55°C and 15min sonication

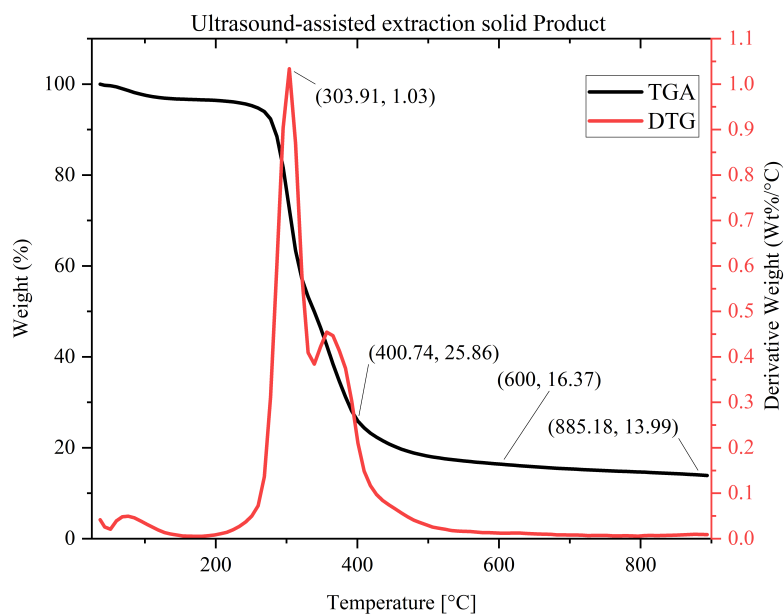


Figure C.4: TGA and DTG of extracted Solid Product of UAE at 55°C and 15min sonication

Enzyme-assisted extraction using Pectinase and ethanol as solvent

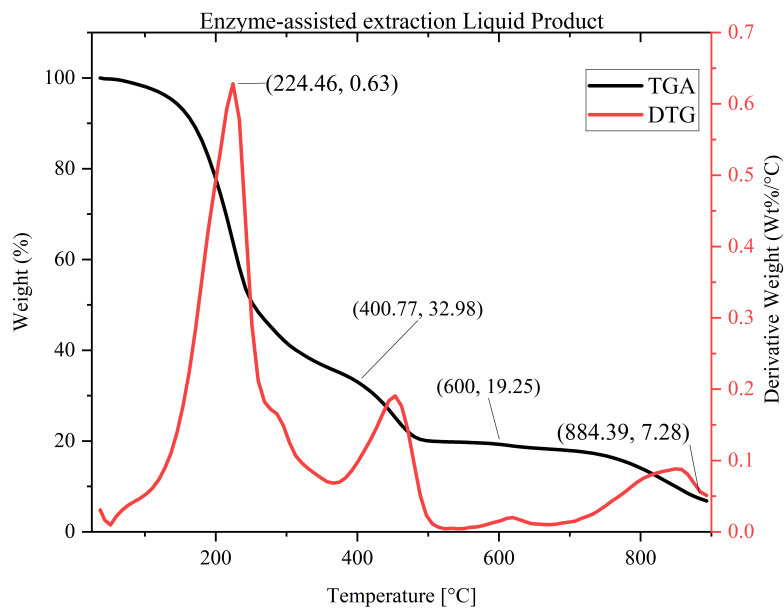


Figure C.5: TGA and DTG of extracted liquid Product of EAE at 55°C and 15min sonication

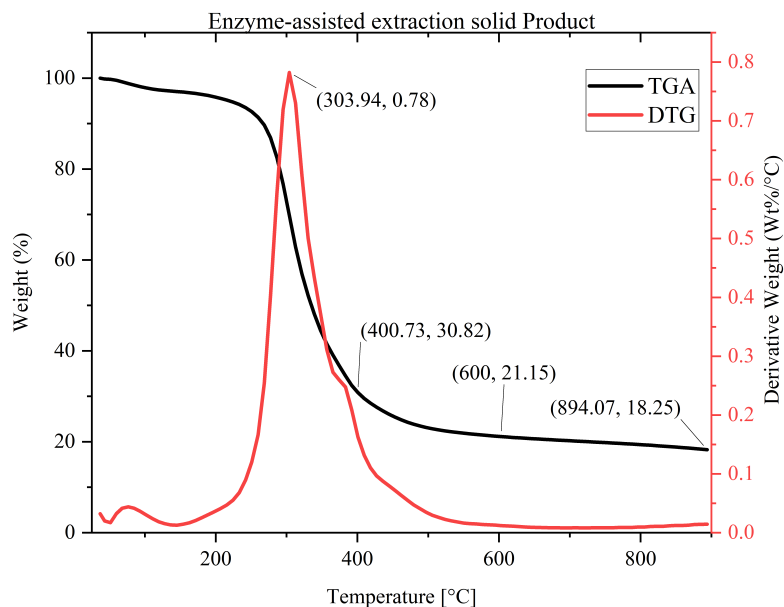


Figure C.6: TGA and DTG of extracted Solid Product EAE at 55°C and 15min sonication

Hybrid Extraction using ethanol as solvent

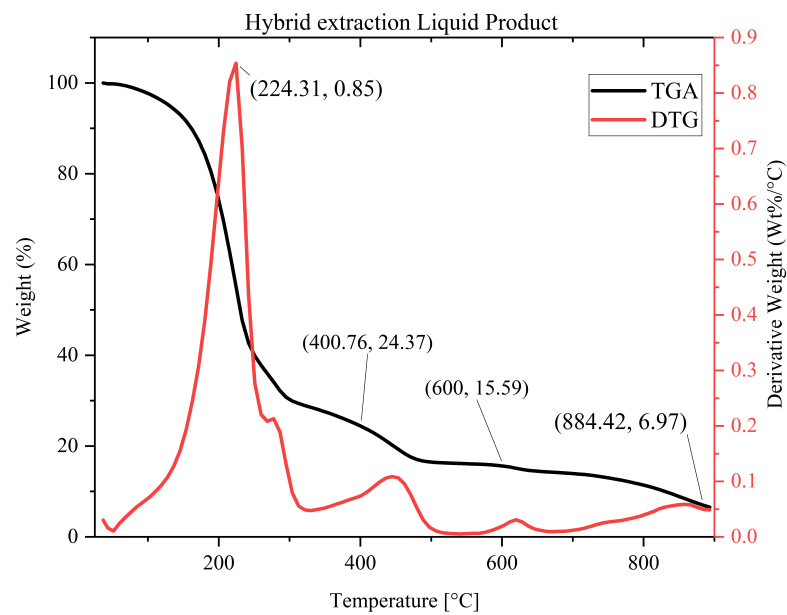


Figure C.7: TGA and DTG of extracted Liquid product of hybrid extraction

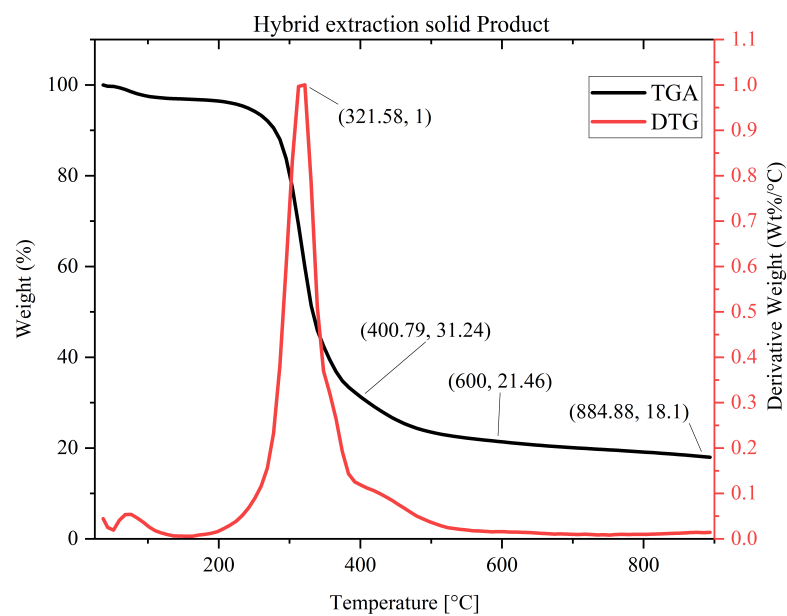


Figure C.8: TGA and DTG of extracted solid product of hybrid method

Equations Used

Moisture

$$Moisture = \frac{\text{Initial weight} - \text{Final weight}}{\text{Initial weight}} \times 100\% \quad (\text{C.1})$$

Oxygen calculation

$$Oxygen(O)[wt\%] = 100 - \sum(CHNS + ash) \quad (\text{C.2})$$

High heating value[12]

$$HHV(MJ/kg) = (0.3289 + 0.0117(100 - C)^{0.25})C + 1.129(H - \frac{O}{10}) + 0.105S \quad (\text{C.3})$$

$$\text{Moles of Carbon} = \frac{\text{wt\% of Carbon}}{12 \times 100} \quad (\text{C.4})$$

$$\text{Moles of Hydrogen} = \frac{\text{wt\% of Hydrogen}}{1 \times 100} \quad (\text{C.5})$$

$$\text{Moles of Oxygen} = \frac{\text{wt\% of Oxygen}}{16 \times 100} \quad (\text{C.6})$$

Product Yield

$$Yield = \frac{\text{weight of product}}{\text{weight of feedstock}} \times 100 \quad (\text{C.7})$$

Note:

The pectinase enzyme was aqueous solution of 1.1 g/ml density. In experiments when the enzyme was used, the residual weight of enzymes would account for approximately 66% of the initial weight of the enzyme added, which was subtracted from the weight of the liquid product.

Conversion

$$Conversion(\%) = \frac{\text{Weight of solid} - \text{weight of char} - \text{weight of catalyst}}{\text{weight of feed}} * 100 \quad (\text{C.8})$$

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