Abstract — Conversion of agricultural residues into valuable products has become an important study in the industry. Generally, they are made up of lignocellulose biomass which requires a particular method such as pretreatment to enhance the desired yield to produce the end product. However, pumpkin is commercialized in very little way in Malaysia, and their processing generates tons of seeds and peels as byproducts. Not to mention the fact that pumpkin wastes have many beneficial nutrients and dry matter that can be utilized in many ways. Pumpkin peel is particularly rich in glucose content and can be converted through several main steps in bioethanol production; pretreatment, enzymatic saccharification, and fermentation which usually uses fungi to obtain fermentable sugar and followed by distillation. Furthermore, bioactive compounds such as carbohydrate, protein, minerals, fatty acid and a significant value on antioxidant compounds like tocopherol, phenols and carotenes are also found in pumpkin seed. On top of that, pumpkin seeds and peels contain quite an amount of pectin that can be extracted through acid hydrolysis and have great potential as gelling agents and thickeners in the food industry as an alternative source from the commercial pectin. These have proven that the usage of pumpkin residuals not only it can provide good benefits to human, in fact, various valuable products can be produced in a cheaper and sustainable way.

Keywords — Lignocellulose biomass, pumpkin byproducts, fermentable sugar, bioactive compound, pectin

I. INTRODUCTION

In recent years, considerable attention has been given to the idea of sustainable and environmentally friendly economic systems, including the use of lignocellulosic biomass in the production of various commodities. Lignocellulosic biomass is classified as the most promising renewable feedstock to produce bioenergy and biochemicals as they are easily available and economical. In fact, the technologies required to produce biomass fuel are cheaper than that of fossil fuels. In 2015, Guilherme [1] studied the pretreatment of sugarcane bagasse, a by-product of the sugarcane industry, to produce glucose, xylose, ethanol, and methane. Lignocellulosic biomass is mainly composed of complex carbohydrates (cellulose and hemicellulose) and aromatic polymer (lignin), where they become recalcitrant to many chemical reactions and limit their uses to produce various goods. However, these compositions are different according to their origin, species and type of biomass.
Generally, biomass source comes from agricultural byproducts such as leaves, seeds, peels, stems etc. Pumpkin belongs to the Cucurbitaceae family, of which its flesh is consumed or used in certain Malaysian cuisines such as masak lemak labu and pengat labu, whilst the seeds, peels, stalks and pods are usually discarded as waste. In Malaysia, pumpkin commercialization is limited due to market demands as pumpkin is mainly consumed fresh by the consumers [2]. According to Norshazila [3], pumpkin in Malaysia is from Cucurbita moschata and Cucurbita moschata duchesne species, and they are both known as labu manis and labu loceng, respectively by the locals. Considering pumpkin’s wastes are full of beneficial nutrients and dry matter, Nwajiobi [4] carried out research on a comparative study on microcrystalline cellulose isolated from fluted pumpkin’s pod husk and stalk. Their findings on the composition of cellulose, hemicellulose and lignin of fluted pumpkin’s pod and stalk are summarized in Table 1.

<table>
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<tr>
<th>TABLE I</th>
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<tbody>
<tr>
<td><strong>Parameter</strong></td>
<td><strong>Pod husk (Parts %)</strong></td>
<td><strong>Stalk (Parts %)</strong></td>
<td></td>
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<tr>
<td>Cellulose</td>
<td>49</td>
<td>41</td>
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<td>Hemicellulose</td>
<td>26</td>
<td>24</td>
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<td>Lignin</td>
<td>9</td>
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Based on Table 1, high cellulose content in both fluted pumpkin pod and stalk can be utilized as feedstock to produce a wide variety of uses, such as alternative sources in sugar production. As in 2017, pumpkin plantations in Malaysia are mostly located in Kelantan, Terengganu, and Pahang, covering around 1531.36 hectares of the pumpkin-producing area [5]. Kamarubahrin [6] studied Malaysia’s overview as prophetic fruits planting hub and reported that Malaysia grows up its pumpkin with considerably large areas of production to meet the increasing global demand. However, pumpkin is still considered an underutilized crop in Malaysia. Thus few recent studies have been conducted on the potential commercialization of pumpkin flesh due to its antioxidant properties and other biologically active compounds [7, 8]. Among the pumpkin-based products available in the Malaysian market are pumpkin powder, snacks, animal feed and pharmaceutical products [8]. Therefore, this paper aims to review valuable products derived from pumpkin wastes.

II. BIOETHANOL PRODUCTION

Recovering industrial and reducing the dependency on other sources to produce various commodities, wastes from pumpkin processing industries could be used as raw materials to produce bioethanol. Meenakshi [9] stated that ethanol is produced from renewable sources such as sugar beet, sweet potato, sweet sorghum or from cheap cellulosic feedstocks like wheat straw, wood, and switchgrass. Bioethanol obtained from lignocellulosic material is classified as “second generation” bioethanol [10]. Generally, biomass conversion into bioethanol involves several main steps, including pretreatment, saccharification, fermentation, and distillation [11]. Figure 1 shows a general procedure to produce bioethanol from biomass waste.

From the figure above, among the main steps involved in pretreatment, which has been conducted at the initial stage, is to enhance the number of obtainable cellulose substrates. This can be done by treating the biomass samples with either physical, chemical or biological pretreatment. This is because cellulose and hemicellulose are potential sources of fermentable sugar. Lignin in lignocellulose biomass provides further strength to the cell wall as well as curbs the enzymatic attack on these complex structures. Hence, pretreatment is a crucial process to cause disruption of lignin and alteration of the crystalline structure of cellulose to make it more vulnerable to enzyme activity to produce the desired products. Dilute acid pretreatment is the most preferred to
pretreat biomass as it generates the least inhibitory compounds throughout the process [12, 15]. Next, for hydrolysis or saccharification, it is a process where lignocellulose or starch-based material is hydrolyzed into their constituent monomer sugar using either acid or enzymes. Then, the process is proceeded with fermentation, where bacteria/fungi such as Saccharomyces cerevisiae are used to ferment the sugar substrates, thus producing ethanol. Lastly, distillation is carried out to separate fermented ethanol and water mixtures by applying heat treatment [16]. Since ethanol will evaporate first, it will condense and be collected in another vessel.

Several studies have suggested that converting pumpkin by-products into renewable energy could reduce pollution in the environment. Chouaibi [11] studied the production of bioethanol from pumpkin peel using different statistical modelling methods, which included Response Surface Methodology (RSM) and Artificial Neural Networks (ANN). RSM is a modelling tool to measure the effects of many independent variables and the response of the experiment whilst, ANN is a well-known feature to measure the non-linear relationships between different parameters and the response of the experiment [17]. In the study, they found that there is around 84.36g/L reducing sugar after being hydrolyzed with amylglucosidase enzyme followed by the production of 50.60g/L of bioethanol after the fermentation process using Saccharomyces cerevisiae. They also found a high starch content in pumpkin peel, which is 65.30%, followed by fiber, water, protein, ash, and a traceable amount of fat. This data indicates that pumpkin peel could be a useful source of glucose.

A previous study by Das [18] on optimization of enzymatic saccharification using RSM and ANN on water hyacinth biomass (WHB) also has been carried out to produce bioethanol. Water hyacinth is an aquatic plant that can be a good source of biomass due to its’ low lignin content [19]. However, in the study, even though alkaline pretreatment was conducted using sodium hydroxide, able to delignify almost 86.76% of lignin content in the WHB, the highest amount of ethanol produced is only 10.44 g/L where the WHB is fermented using Pichia stipitis. Thus, the highest amount of ethanol produced from WHB still does not achieve half of the theoretical ethanol yield as predicted by the researchers. Despite the low lignin content offered by the aquatic plant, WHB however has the ability to decompose dissolved oxygen in the water thus threatening the aquatic system in the river [20]. Therefore, the selection of biomass resources such as WHB should be taken into account to reduce hazards that this plant likely will cause in the final product of bioethanol. Other than that, enzyme hydrolyzed WHB from this study shows that it can only produce 24.5% and 34.1% of fermentable cellulose and hemicellulose, which are much more little as compared to cellulose from pumpkin’s wastes.

Recently, Yesmin [21] conducted a study on bioethanol production from renewable resources using rotten corn, pumpkin and carrot in Bangladesh. In their study, two varieties from pumpkin, Cucurbita maxima L., were used, which are black pumpkin and red pumpkin. After the fermentation process using Saccharomyces cerevisiae, a higher bioethanol yield was produced from the red pumpkin, which is 53ml ethanol with 6% (v/v) purity compared to only 40ml of ethanol with 4% (v/v) purity from the black pumpkin. Moreover, the high sugar content was also found in red pumpkins (7.63 mmol/L), which is comparatively higher than the black pumpkin (5.46 mmol/L). In this study, the addition of α-amylase enzyme in all substrate solutions is said able to speed up the fermentation process. Besides, the selection of pumpkin as raw material in bioethanol production is due to its storage shelf life can up to 6 months before consumption [21]. This suggests that pumpkin can be a good source of raw materials to produce bioethanol, too, due to its lignocellulose content that is renewable and non-competitive with other food crops [22].

Other than rotten pumpkin, starchy biomass such as potato peel also has been used as feedstock to produce bioethanol. In 2018, Malik [23] studied on optimization of conditions for bioethanol production from potato peel. Under controlled parameters of temperature, pH, and incubation period using different methods to optimize the conditions, four yeast species were used in Separated Hydrolysis Fermentation (SHF) and able to produce 2.83% ethanol after 72h. In contrast, around 3.75% of ethanol was produced using Saccharomyces cerevisiae in the Simultaneous Saccharification and Fermentation (SSF) method in a shorter time of 48h. The principles of SHF and SSF are different where enzymatic hydrolysis and fermentation are performed separately in SHF, whilst in SSF, both processes are performed simultaneously. SSF method produced low inhibitory end products and low cost [24]. Thus, SSF gives a better performance to produce a higher yield of ethanol in a rapid time as compared to SHF [23][25]. However, the yield of ethanol from potato peel waste is still less favorable due to low production and less efficiency compared to ethanol from pumpkin wastes.

### III. BIOACTIVE COMPOUNDS DERIVED FROM PUMPKIN WASTE

The utilization of pumpkin is varied according to the culture and needs of particular places. For instance, in Nigeria, pumpkin is grown for the purpose of living without the need for commercialization [26]. Nigerians make use of pumpkin in a traditional method as a cover crop and weed control agent. In the USA, pumpkins are immensely used for the thanksgiving feast and cravings [27]. Whilst, in Malaysia, pumpkin plantation is mainly for domestic consumption and export purposes, according to a Senior Agronomist Expert, Hosnan [28]. Conversion of pumpkin byproducts produced during production, processing, preparation and distribution into sustainable goods is to preserve the loss of biomass and valuable nutrients such as bioactive compounds available in the wastes. In general, pumpkin seeds are regarded as agro-industrial wastes even though they are eaten raw, roasted or cooked in some other countries but only on a small scale [29]. Bioactive compound found in pumpkin waste is a type of substances that possess biological activity in metabolic reaction that could promote good health in human body. Therefore, this section will discuss on bioactive compounds derived from pumpkin seeds and other pumpkin parts:
A. Nutritional Composition of Pumpkin Waste

Pumpkin seeds are a good source of fat, protein, carbohydrates and minerals. According to a database provided by FoodData Central [30], 100g of pumpkin seed contains 30.25g protein and 49.05g total fat. The highest mineral and vitamin contents are phosphorus and vitamin E, respectively. Devi [31] stated that pumpkin seeds play an important role in providing essential nutrients against various diseases such as arthritis, inflammation and prostate cancer. Furthermore, they can be routinely eaten without having any side effects on one’s health [32]. Elinge [33] reported a study on the analysis of chemical composition and mineral content of pumpkin (Cucurbita pepo L.) seeds extract in 2012. They revealed that the most abundant element in the seeds is potassium, and the least is manganese. In their study, the concentration of lipid, carbohydrate and protein has been found to be the highest, which are 38.00%, 28.03% and 27.48%, respectively, in the samples.

Rezig [34] carried out a proximate analysis and fat extraction on pumpkin (Cucurbita maxima) seeds, and they found a significant value on seed’s chemical composition, which comprises 8.46% moisture, 33.92% protein, 3.97% fiber, 21.97% ash, 31.57% lipid and 0.11% total sugars. High lipid content in this study is similar to the findings from a study by Veronezi [35] in 2012, of which they determined 30.68 to 42.29% of lipid content in the varieties of pumpkin seed samples. Besides, oleic acid was also found to be the highest percentage in the seeds, which is 44.11%, followed by linoleic and palmitic acid with 34.77% and 15.97%, respectively and these major fatty acids are also found in the study conducted by Massa [36]. Another study on chemical composition and nutritional values in various pumpkin species (Cucurbita maxima, C. pepo, C. moschata) and parts (seed, peel, flesh) from Korea have been conducted by Kim [37]. From the results, seeds from all varieties of pumpkins significantly contain the highest amount of carbohydrate, protein, fat and fiber compared to peel and flesh. Furthermore, using Fatty Acid Methyl Ester (FAME) analysis to determine fat content in the samples, Kim and colleagues found a high percentage of polyunsaturated fatty acid in the seeds of all pumpkin species. A high level of unsaturated fatty acid (oleic and linoleic acid) in pumpkin seeds could help to improve blood cholesterol levels, regulate heart rhythm and relieve inflammation [38].

B. Antioxidant Activity

Nowadays, there is an increased interest in natural antioxidants derived from pumpkin materials. Therefore, many studies have been conducted on the antioxidant activity in pumpkins, such as in pumpkin flowers, leaves, seeds and recently in pulp by Kulczyński [41]. Properties of antioxidants are measured by the capability of antioxidant compounds such as phenols, flavonoids, beta-carotene, alkaloids and other phytochemicals or vitamin antioxidants to scavenge free radicals and reactive oxygen species (ROS). Oxidative stress is caused by the unbalanced formation and neutralization of prooxidants molecules often associated with chronic diseases in humans [42].

Saavedra [43] previous study in 2013 evaluated antioxidant properties in pumpkin seeds and shells using different extraction solvents and drying methods. Around 18.92-70.96% inhibition against 2,2-diphenyl-1-picrylhydrazyl, DPPH free radicals was found using 70% ethanol on both seeds and shell samples. There are significant differences in inhibition of DPPH radicals in different drying methods. The oven-dried (65°C) samples showed 2.65-72.36% inhibition, while the freeze-dried samples exhibited 1.47-52.41% inhibition. In
2017, Peiretti [44] investigated the antioxidative activities and phenolic compounds of pumpkin (Cucurbita pepo) seeds and amaranth (Amaranthus caudatus) grain. The samples were extracted using 80% (v/v) methanol, and they found that pumpkin’s extracts contain a higher total phenolic compound (TPC) than amaranths. Whilst, Veronezi and Jeorge [35] studied the bioactive compounds in four varieties of pumpkin (Cucurbita sp.) seeds; Nova Caravela, Mini Paulista, Menina Brasileira and Moranga de Mesa. According to their findings, Mini Paulista contains the highest total phenolic compound with 3.62mg EAG/g, followed by Nova Caravela, Menina Brasileira and Moranga de Mesa with 3.56, 2.39 and 1.35mg EAG/g, respectively. Moreover, among the varieties of pumpkin, the Mini Paulista seed and its lipid fraction contain the highest carotenoid levels compared to other seeds’ varieties. These findings suggested that pumpkin seeds and shells possessed a good antioxidant property that benefits human health by preventing the accumulation of free radicals that contribute to the development of degenerative diseases such as autoimmune disorders, aging, arthritis, prostate cancer [45] and other chronic illnesses.

A study on the uses of carrot (Daucus carota L.) and pumpkin (Cucurbita pepo. L.) by-products such as bark and peel to increase nutritional compound in extruded crispbreads products are described by Konrade [46]. Other than producing a soft and crispy crispbread, the fortification of carrot and pumpkin by-products in the wheat flour dough is to measure the amount of added nutrients in the final product. Initially, total carotenes measured using a spectrophotometer found that dried powdered pumpkin wastes contain a higher amount of carotene compared to carrot wastes. After the addition of 20% of carrot and pumpkin by-products into the ingredients, carotene content in the samples fortified with pumpkin was significantly increased from 0.77 ± 0.01 mg/100g to 6.51 ± 0.02 mg/100 g compared to only 1.60 ± 0.01 mg/100g in samples fortified with carrot. Lutein was identified comes from a pumpkin that is highly thermal stable [46]. According to Obрадовић [47], the sensitivity of carotenoids to heat treatment highly depends on their source. Thus, carotenes from pumpkin are suitable to be added in food products that undergo high heat treatment. Besides, dietary fiber measured in the samples added with pumpkin by-products was slightly higher than samples fortified with carrots. Consumption of food with high dietary fiber may promote a smooth digestive system and regulate bowel movements in humans [48].

IV. ALTERNATIVE SOURCE FOR PECTIN PRODUCTION

Other than bioactive compounds, waste materials from the pumpkin processing industry also contain a significant amount of pectin, which can be derived and applied in food products. Pectin is a natural heteropolysaccharide, a component of the primary plant cell wall located in the middle lamella that is composed of acidic sugar-containing backbone and neutral sugar-containing side chains [49]. They are mainly made up of galacturonic acid that is linked together by α-1,4 glycosidic bonds. According to Mellinas [50], the carboxyl groups of uronic acid residues can be present in different forms in the polymer structure, either free or as a salt form with sodium, calcium or other small counter-ions. However, Srivastava and Malviya [51] reported that the structure and composition of pectin are varied between plants in different parts.

Currently, commercial pectin is derived from apple pomace and citrus peel. The ability of pectin to increase viscosity and bind with water has made it a gelling agent in jam and jellies. Besides, it is also used as a stabilizer in fruit juice and milk. Xiao [49] stated that pectin’s complex structures are vulnerable to the degradation of enzymes and the fact that plant biomass consists of several different hexoses and pentose polysaccharides. Therefore, biomass samples, including pumpkin waste, must be treated with acid hydrolysis first prior to pectin extraction. Acid hydrolysis caused cleavage of glycosidic bond in pectin polysaccharide to produce galacturonic acid, thus enhance the pectinase activity on pectin structure during extraction. Figure 4 summarized the pectin production from processing of biomass wastes up to its analysis methods.

In 2019, a study was carried out by Dona [53] on the pumpkin (Cucurbita maxima) from Sri Lanka. The researcher extracted pectin from pumpkin parts (whole fruit, core and peel) according to different parameters; blanching methods, acid types, extraction time and temperature. Pectin yield was found to be the highest (2.91%) in peel when the samples were subjected to acid treatment using hydrochloric and citric acid. It seems that the hard part of the pumpkin contains more pectin compared to its’ internal parts. The ability of pectin to form gel is highly influenced by the degree of esterification (DE), where
DE is measured according to methoxy content in pectin. In detail, DE more than 50% is considered as high methoxy and vice versa [54]. From this study, Dona found that the DE of pumpkin pectin is 67.64, thus shows that pectin extracted from pumpkin has the potential as gelling agent and thickeners in the food industry.

A study on pectin characterization from selected non-citrus fruit wastes in Nigeria have been carried out by Ogunka-Nnoka [55], where the varieties of non-citrus fruits are; Telfairia occidentalis (Pumpkin seed peel-psp), Telfeira occidentalis (Pumpkin seed white pod-pwp), Artocapus camanis (Breadfruit seed peel-bp), Artocarpus camansi (Breadfruit creamy pulp-bcp) and Mucuna urens (Horse eye bean peel-hbp). Figure 5 illustrated the percentage of pectin produced after being treated with nitric acid in all samples:

The results showed that pectin content from hbp was the highest, ranging in 1.09-4.40%, whilst bcp had the lowest pectin content (1.00-2.80%). However, further analysis was carried out on the degree of esterification (DE), and the percentage of anhydronic acid (AUA) found that wastes from pumpkin (psp and pwp) were significantly high. According to Ahmad and Sikder [56], AUA indicates the purity of pectin content in the samples. Results of DE on psp is 71.47% which also showed that psp has high methoxy content and slightly less than the commercial pectin, 77.50% [53]. On top of that, another waste from pumpkin, which is pwp has the highest AUA, which is 20.78% purity content compared to other samples. This evidence showed that pumpkin wastes have great potential as an alternative source of pectin to be commercialized as thickeners in jam or jellies in the future.

Lalnunthari [57] reported on the extraction of protein from pumpkin seed and pectin from pumpkin peels to formate edible films and their optimization using Respond Surface Methodology (RSM). According to Cerqueira [58], edible film is a type of edible coating material used as packaging or wrap to protect food and food components. They can be prepared by incorporating proteins, polysaccharides, pectin, lipid as a film. Under the optimized condition of 89.98 °C extraction temperature, 13 minutes extraction time and pH of 2.85, Lalnunthari found 69.89 ± 2.90% pectin yield from pumpkin peels. Pectin yield is directly proportional to the extraction temperature and time due to the higher reaction rate for mass transfer of pectin from the sample to the extracting solution (sodium hydroxide). However, it seems that the pH of the peel sample is low to provide acidic conditions and able to solubilized pectin. Hence more pectin is produced. As for the edible film, incorporation of both extracted protein and pectin from pumpkin wastes was successfully produced a good property of the film. However, overall, some improvements on the proportion of materials need to be implemented to produce a more quality film. Erkmen and Barazi [59] mentioned that materials used to make edible film must be as thin as possible with adequate mechanical properties to protect food components and have the capability to limit the transfer of gas and water vapor between food material and the outer environment.

V. CONCLUSIONS

Bioconversion of pumpkin wastes has garnered attention due to the fact that these residuals contain a useful and utilisable resource to be transformed into valuable products. The purpose of this review paper is to provide an overview of pumpkin wastes commercialization as feedstock in producing valuable products. These include the synthesis of bioethanol, bioactive compounds derived from pumpkin material and pumpkin wastes as an alternative source to produce pectin. The aforementioned research studies show that pumpkin wastes such as peels and seeds have a great potential to be used as raw materials for many uses; however, the recalcitrance of biomass structure in pumpkin wastes gives an impact on the amount of obtainable yield. Thus, they need a suitable pretreatment method to enhance the production of the desired compound, such as cellulose. In the future, studies on the optimization of the pretreatment method to capture the full content and valuable lignocellulosic material from pumpkin wastes need to be carried out. This also includes the study in the utilization of pumpkin waste as feedstock in the production of bioethanol as there are not many studies have been conducted on pumpkin wastes compared to other biomass such as potato waste, corn, etc.

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