Potential of durian, avocado and jackfruit seed as raw material of bioethanol: a review

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Abstract. The using of fuel oil is very consumptive so that it increases every year, as decreasing the availability of non-renewable natural resources, therefore the use of alternative energy (renewable energy). Renewable energy is a natural source of energy produced that will not be exhausted and can be sustainable if managed properly, among another biofuel. The purpose of this article to review the potential of tropical fruit seeds: durian, avocado, and jackfruit as raw materials for bioethanol production include stages: starch extraction, hydrolysis process using acid as catalyst, and fermentation. From available research data, the potential of tropical fruit seeds needs to be developed as raw material for making bioethanol.

1. Introduction
The demand for fuel oil always increases while the production decreases, due to the availability of natural resources [1], to make demand renewable energy has been looked at as a new source. Renewable energy is a naturally occurring source of energy that will not be exhausted and can be sustainable if managed properly: such as biofuel, biomass, biogas, etc [2][3][4][5]. The development of biofuels in Indonesia needs to be done according to the government policy outlined in the "National Energy Policy" on the utilization of biofuels targeted 5% in the 2025 year [6].

Current famous biofuel products are bioethanol. Bioethanol is the result of the sugar fermentation process with carbohydrate source (starch) using microbial activity. The fermentation process usually does not use oxygen (anaerobic process). Raw materials for bioethanol production Generally classified into three groups: sugar, starch, and cellulose. Sugar such as cane sugar, beet sugar, molasses, and fruits contain high levels of glucose: bananas can be directly converted to bioethanol by the fermentation process. The raw materials such as starch/cellulose such as corn starch, potato, cassava, and fruits waste, and others, must be hydrolysed before further fermentation process to be converted into bioethanol [7].

Starch-based bioethanol should be avoided as it interferes with food security [8]. Materials containing high cellulose and starch from Durian, Jackfruit, Cempedak, and Avocado seed are alternative for bioethanol [8][9][10][11]. The seeds of durian, Jackfruit and Avocado are discarded and untapped they are the content of starch and cellulose from the seeds is high so that potential material for bioethanol. This article aims to review the potential fruit seeds durian, avocado, and jackfruit as raw material for bioethanol production including starch extraction and hydrolysis and fermentation.

2. Production of starch-based bioethanol production from tropical fruit seeds.
Bioethanol is production through starch extraction, hydrolysis, and fermentation. Stages (figure 1)
2.1 *Starch extraction.*
This starch extraction aims to obtain high starch flour which is used as a raw material of bioethanol manufacture before entering the hydrolysis and fermentation process stage. The starch of extraction from tropical fruit seeds using water solvent, alkali and enzyme [9][10][12][13][14].

2.1.1 *Water solvent.*
The seeds were washed and rinsed and then dried under the sun for 6 hours. The fruit seeds are cut thinly [9][15][17] with a thick of ± 2 mm [17] to ease the seeds into the slurry. Thin seeds were mixed with water (1: 5; w/v) and blended to form a slurry [18]. It has been seed homogeneously stirred, precipitated in gravity for 3-24 hours, filtered and the filtrate was taken [8]. The starch was dried using the oven at 50°C [19, 20] for ± 24 hours until dry. The dried of starch was ground and sieved to a size of 100 mesh [21].

2.1.2 *Alkaline.*
This method of seed is mashed into flour, 5 g of flour was added a solution of NaOH with concentration variations (0.1, 0.25, and 0.5%) soaked (6 hours and 8 hours) at room temperature and continuous stirring. Starch slurry is filtered through 212 mesh sieve filter. The remaining sediment was washed with distilled water for 3 times. The filtrate is combined and precipitated for 24 hours at 40°C. The supernatant is removed and starch is cleaned using distilled water. This procedure was repeated three times, the starch flour was dried at 40°C for 24 hours in the oven. The dried starch is ground with
a mortar and pestle. Starch is packed in plastic bags and stored at room. The optimum condition of this method is at 0.5% NaOH and 6 hours of immersion [13].

2.1.3 Enzymes.
A total of 5 g of seed flour was added to (α-amylase) with various concentrations (0.1 g, 0.25 g, and 0.5 g) and soaked into 100 ml of water at room temperature for 6 hours and 8 hours and stirred continuously. The pH of the solution is maintained at 6.0. The slurry is filtered through a 212 mesh sieve filter. The remaining sediment was washed with distilled water for 3 times. The filtrate is combined and precipitation a long 24 hours at 40°C. The supernatant is removed and the starch is cleaned with distilled water. These steps are repeated three times and the starch is dried at 40°C for 24 hours. The dried starch was ground with a mortar and pestle. Starches are packed in plastic bags and stored at room temperature until further use. The optimum condition of this method was at 0.25 g of enzyme and immersion for 6 hours [13]. Seeds-based starch extraction research such as durian, jackfruit and avocado seeds using water solvent method, alkali and enzyme solution affected by the time of precipitation of starch, the following are extraction methods, the precipitation time and the yield starch presented in table 1.

### Table 1. Extraction of seed-based starch using water solvent, alkali and enzyme method.

| Extraction of method | Sample | Precipitation time (h) | Starch yield (%) | Reference |
|---------------------|--------|------------------------|-----------------|-----------|
| Water solvent       | 100 g slurry of avocado seed | 24 | 24.2 | [12, 22] |
| Sodium meta bisulphate solution 0.2% | The slurry of jackfruit seed | 24 | - | [23] |
| Water solvent       | 5 g jackfruit seed | 5.24 | 84.48 | |
| NaOH solution 0.5%  | 5 g jackfruit seed | 6-8 | 57.34 | [13] |
| α amylase enzyme    | 5 g jackfruit seed | 6-8 | 52.74 | |
| NaOH solution 2%    | Jackfruit seed | 24 | - | [24] |
| Water solvent       | 100 g slurry of durian seed | 24 | 20.48 | [9] |
| Water solvent/oil (30%:70%) | 100 g slurry of durian seed | 1 | 58.80±7.32 | [25] |
| NaOH solution 0.5%  | Jackfruit seed | 2 | 20.12 | [26] |

Table 1: Should data yield of starch produced in starch extraction tropical fruit seeds using a greater water solvent than using chemical compounds or enzymes. In general, the deposition time required for extraction using chemical compounds or enzymes is smaller than using water solvents. reported that as much as 5 g of jackfruit seeds extracted using a water solvent required a 6-8 hour deposition time to produce 84.48% yield starch [13]. Reported that as much as 100 g of durian fruit pulp was extracted using water/oil (30/70) it took 1 hour to settle to produce 58% yield starch [25]. Reported that extracting jackfruit seeds using 0.5% NaOH solution required 2 hours of settling time to produce 20.12% yield starch [26]. Reported that as much as 100 g of jackfruit seed pulp extracted using water needed 24 hours to produce 24% yield starch [8,18]. Reported that as much as 100 g of durian pulp seed extracted using water required a settling time of 24 hours to produce 24.48% yield starch [9]. extracting jackfruit seeds using 2% NaOH solvent required 24-hour deposition time [24]. extract jackfruit seeds using Sodium meta bisulfate solution 0.2% required 24-hour deposition time [23].

Extraction using a water solvent takes time to precipitate all starch from the tropical fruit seeds slurry about 1-24 hours. This precipitation time is affected by the specific gravity of the starch slurry mixture. Yield starch obtained 20-84%. The value of yield is influenced by the amount of starch contained in the seeds. The process of reducing seed size to forming slurry by scraped or mashed determines the value of starch yield. The method of extraction using the NaOH or enzyme solution.
compounds also affects the resulting yield value. Chemical compounds can remove starch from the grains by 20-57% with a settling time of about 1-8 hours [9, 13, 22].

2.1.4 Starch characterization.
The starch characterization aims to determine the percentage of chemical components contained in starch. The includes starch, moisture content, ash, fat, protein, amylose, and amylopectin content in avocado, durian, and jackfruit are presented in table 2.

Table 2. Characterization of starch-based tropical fruit seed: avocado, durian, and jackfruit.

|                  | starch/amylum (%) | amylase (%) | amylopectin (%) | water (%) | ash (%) | fat (%) | Protein (%) | Reference |
|------------------|-------------------|-------------|-----------------|-----------|---------|---------|-------------|-----------|
| Durian seed      | 76.653            | 22.336      | 54.316          | 14        | 0.13    | 0.07    | 0.81        | [9]       |
| Durian seed      | -                 | -           | -               | 5.32      | 0.3     | 0.68    | 4.25        | [27]      |
| Avocado seed     | 73.62             | 0.07        | 73.55           | 16.6      | 0.23    | 1.09    | 2.16        | [12]      |
| Jackfruit seed   | 92.8              | -           | -               | 0.07      | 0.16    | 0.59    | 7.98        |           |
| Jackfruit seed   | 94.5              | -           | -               | 0.07      | 0.67    | 0.24    | 5.56        | [23]      |
| Jackfruit seed   | -                 | 49.96       | 50.54           | 11.18     | 0.33    | 0.27    | 0.88        | [26]      |
| Jackfruit seed   | 81.05             | 26.49       | -               | 9.02      | 2.66    | 1.4     | 11.34       |           |
| Jackfruit seed   | 82.52             | 30.21       | -               | 9.16      | 1.53    | 1.32    | 9.75        | [13]      |
| Jackfruit seed   | 81.32             | 30.09       | -               | 6.28      | 2.51    | 1.18    | 9.19        |           |

Table 2 showed the research of starch content of tropical fruit seeds: durian jackfruit and avocado amount 81- 94.5%. High starch content is good using at the hydrolysis process stage to produce glucose. According to Mandruga, et al 2014 jackfruit seeds of hard varieties contained the highest starch content of 94.5% [23]. Its content of tropical fruit seeds has met the requirement of Indonesia Industrial Standards starch which is minimal 73% so that it is allowed for food industry based on starch and especially raw material of hydrolysis produce glucose

2.2 Hydrolysis

Hydrolysis is a process of a chemical reaction (decomposed) a compound using water [27] to produce a new substance. According to Groggins, reactions of hydrolysis require heat/endothermic reactions [27]. Hydrolysis of seed starch-based breakdown macromolecule chain (polymer) into the smallest units/droplets ($C_6H_{12}O_6$) following the reaction

$$\text{Starch} + x \text{H}_2\text{O} \rightarrow x \text{C}_6\text{H}_{12}\text{O}_6$$

(1)

The process of termination of the polymer bond to form the starch chemically, enzymatically or a chemically-enzymatic combination. Chemically hydrolysis usually using a dilute acid solution as a catalyst, such as HCl or H$_2$SO$_4$ with a concentration of 2-5% at a reaction temperature of ± 160°C [7][30]. Enzymatic hydrolysis involves the aid of certain microorganisms. Hydrolysis of starch enzymatically is the saccharification process, which breaks the entire macromolecule starch produced by glucose. The most commonly used enzymes are α-amylase, β-amylase and glucoamylase [7][30][29][30]. Research data of hydrolysis of starch-based starch of tropical fruit seed chemically, enzymatically and the chemically-enzymatic combination is presented in table 3.
Table 3. Research hydrolysis of starch-based tropical fruit seed is chemically, enzymatically and chemically and enzymatically combined.

| Method                        | Sample                  | Catalyst/ enzyme | Hydrolysis temperature | Hydrolysis time | Glucose levels | Reference |
|-------------------------------|-------------------------|------------------|------------------------|-----------------|---------------|-----------|
| Chemically                    | avocado seed powder     | H$_2$SO$_4$ solution (3%-7%) | 120°C                  | 60 minute       | 17.4%         | [7]       |
| Chemically                    | jackfruit seed solution (w) | HCl solution pH= 2; 3; 3.5; 4 | 135°C                  | 45 minute       | 19.24%        | [29]      |
| enzymatically                 | jackfruit seed solution (w) | amylose α-enzyme (0.3 ml-0.7 ml) | 90°C                   | 30 minute       | 17.36%        | [29]      |
| chemically-enzymatic combination | 100 g mix Cassava and durian seed | H$_2$SO$_4$ solution pH 5 | -                      | 48 hour         | -             | [30]      |
| Subcritical water hydrolysis  | A mixture of durian seed flour-water (%w) | -          | (120°C-160°C)          | (1; 3; 5 hour)  | 9.85 g/ml     | [27]      |

Nuriana and Wuryantoto showed that hydrolysis of jackfruit seed starch using HCl acid catalyst yields bioethanol with higher content (19.24%) than using enzymatic (17.36%). Glucose produced as a reaction product is related to the concentration of reactants, pH, and activation energy ($\Delta E$). The relation product and the reactants can be expressed in the conversion of kinetic model equations of polymerization reactions approaching the first-order reaction equation in accordance with Bej about study of kinetics of hydrolysis reaction of acid-catalyzed [31] influencing activation energy [32] so it is obtained the relationship between product (glucose) with the reactant (starch) to the hydrolysis time associated with the effect of reaction rate constant, activation energy and pH to the hydrolysis kinetics equation.

2.3 Fermentation

The process of decomposition of glucose compounds into ethanol compounds, C$_2$H$_5$OH and CO$_2$ involve the activity of microorganisms/enzymes called alcohol fermentation. Fermentation is usually in an anaerobic state, for example, using yeast or yeast microbes. Fermentation based on grain starch-containing polysaccharide compounds has two stages: the first stage of change of polysaccharide compounds (amyloan and cellulose) into monosaccharides (glucose) with acid catalyst and the second stage is the conversion of glucose into bioethanol with the help of microorganisms [3][7][23][25][26][27]. The reaction process of converting starch into bioethanol as follows:

$$\text{(C$_6$H$_{10}$O$_5$)$_x$ + x H$_2$O} \rightarrow x \text{C$_6$H$_2$O$_6$} \quad \text{step 1}$$

$$\text{C$_6$H$_{12}$O$_6$ (l)} \rightarrow 2 \text{C$_2$H$_5$OH (l) + 2 CO}_2(g) \quad \text{step 2}$$

Some research data of the fermentation process of tropical fruit seed using yeast activity: Saccharomyces cerevisiae presented in table 4.
Table 4. Research of fermentation process tropical fruit seed using yeast activity: Saccharomyces Cereviceae.

| Sample                      | Yeast                          | pH  | Fermentation Temperature | Fermentation Time | Ethanol Levels (%) | Reference |
|-----------------------------|--------------------------------|-----|--------------------------|-------------------|--------------------|-----------|
| The starch of avocado seed  | Saccharomyces cerevisiae 20%   | 4-5 | 120°C                    | 120 hour          | 15.1               | [7]       |
| Durian seed                 | Saccharomyces cerevisiae       | 5   | 140°C                    | 72 hour           | 9.85               | [27]      |
| Jackfruit seed              | Saccharomyces Cereviceae, urea and N-P-K | 3.5 | 135°C                    | 0.5 hour          | 13                 | [29]      |
| 100 g mixe Cassava and durian seed (50:50) | Saccharomyces cerevisiae yeast. | 5   | 35°C                     | 48 hour           | 35.7               | [30]      |
| Artocarpus champeden seed   | Saccharomyces cerevisiae       | -   | 36°C                     | 144 hour          | 8.233              | [11]      |
| Jackfruit seed              | Saccharomyces cerevisiae       | -   | 30°C                     | 144 hour          | 18.98              | [33]      |

Fermented alcohol based on glucose derived from starch is effected substrate concentration, temperature, nutrition, pH and fermentation time [34] [35]. Substrate concentration should be considered, if too large make spurs the mortality rate, while too small yeast productivity will reduction and becoming a tired lead to contamination. Temperature and pH affect the growth of Saccharomyces cerevisiae around 25-35°C and pH conditions (4-6) affecting bioethanol levels. Nutrition also affects the activity of Saccharomyces cerevisiae, in addition to carbon, sources are needed also nitrogen, vitamins (biotin and thiamin) and minerals such as phosphate, potassium, sulphur, and a small amount of iron and copper compounds. The fermentation time for 3-14 days is related to the mortality rate if it is too long whereas if a little bit of bioethanol is produced.

3. Conclusion
Preparation of bioethanol based on tropical fruit seeds starting from the extraction of starch from the seed using water as a solvent, Hydrolysis process with the catalyst of acid followed by a fermentation process using microbial Saccharomyces cerevisiae. Durian, avocado jackfruit seeds are the potential to be as raw material for bioethanol production.

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