The processing of used cooking oil (yellow grease) using combination of adsorption and ultrafiltration membrane processes

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Abstract. Yellow grease is used cooking oil whose quality has degraded due to the oxidation, polymerization, or hydrolysis process. In previous studies, yellow grease refining had been conducted either by adsorption or by using membrane. In this study, adsorption process using adsorbent from bagasse activated with H₃PO₄ 12.5%, and ultrafiltration using Polyethersulfone (PES) membrane were combined. In adsorption stage, several variation of bagasse mass was fed into 200 ml of yellow grease and stirred for 60 minutes at 60 rpm. Yellow grease produced from adsorption with best condition was then processed using ultrafiltration membrane that is PES membran with concentration by 15 wt% with transmembrane pressure variation by 0.5; 1; 1.5; 2; and 2.5 Bar. Analysis of yellow grease characteristics before refined showed its acid number, peroxide number, iodine number, and water content respectively by 2.68 mgKOH/Kg; 5.97 Meq/Kg; 51,48; and 1.29%. Characteristics of yellow grease after adsorption at its best condition on the parameters of acid number, peroxide number, iodine number, and water content are respectively by 2.55 mgKOH/Kg; 4.19 Meq/Kg; 40,02; and 0.27%. Characteristics of yellow grease after ultrafiltration at its best condition on the parameters of acid number, peroxide number, iodine number, and water content are respectively by 1.12 mgKOH/Kg; 1.8 Meq/Kg; 41,36; and 0.02%. Combination of adsorption and ultrafiltration processes for yellow grease processing showed decreasing value on the parameters of acid number, peroxide number, and water content that conforms to the SNI quality standard, but has not been able to increase the iodine number.

1. Introduction
Cooking oil is a medium for frying foods. The purpose of using cooking oil is as a medium for conducting heat in order to change the physical appearance and texture of the foodstuffs that will give savory taste, and also to add nutritional value and calorie in the foodstuffs [1]. Cooking oil which has repeatedly been used and is damaged is called as yellow grease (used cooking oil). The oil damage is caused by oxidation, polymerization, or hydrolysis process during the frying which causes the formation of unwanted carcinogenic compounds (peroxide and aldehyde) that harmful for health.

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Research regarding yellow grease refining has been widely conducted and the methods that are commonly used in between are adsorption and membrane process. Yellow grease refining process is purposed to reduce compounds that were performed due to the oil damaging process [2], and then the refined yellow grease can be utilized as a benefit things such as material for soap and biodiesel. However, the advanced studies is needed to innovate method in refining yellow grease.

Adsorption is a method that is commonly used in refining yellow grease. Adsorption is chosen because its process is easy to perform, and usually is effective in reducing free fatty acid in yellow grease. The previous studies of refining yellow grease using adsorption process were conducted by Muallifah (2009) using activated carbon from moringa oleifera seed; Ramdja et.al (2010) using adsorbent from bagasse; Yustinah and Hartini (2011) using activated carbon from coconut fiber; and Triyanto (2013) using activated carbon from bagasse. Membrane technology has been extensively used for refining of oil [3]. Membrane separation is based on a physical retention of compounds present in treated stream and depend mainly on molecular weight of a separated substance [4]. Membrane process for increasing the oil quality is easy to perform and has many advantages compared to other process, because of its low energy consumption, ability to operate in room temperature, and because the addition of chemicals is not necessary [5]. The previous studies of refining yellow grease using membrane were conducted by Widyaningsih and Purwati (2013) using nata de coco membrane; Miyagi et.al (2003) using nonporous composite membrane; and Subramanian et.al (2000) using various of polymer membranes. In this research was conducted a process combination of adsorption and ultrafiltration, where the adsorption process is on the pretreatment stage that is purposed to reduce membrane workload in ultrafiltration process, so that it can increase the quality of refined yellow grease. The aim of this research was to study the effect of process combination of adsorption and ultrafiltration on characteristics of refined yellow grease. The adsorbent used is bagasse activated with H₃PO₄ 12.5%. The high content of carbon in bagasse after activation become the reason why using bagasse activated carbon in yellow grease refining. The membrane used is Polyethersulfone membrane which is hydrophobic that it suits for processing yellow grease. Characteristics of oil before and after refined are including acid number, peroxide number, iodine number, and water content.

2. Materials and Methods
This study was conducted a process refining of yellow grease that consists of two stages that are adsorption and ultrafiltration processes. The using combination processes of adsorption and ultrafiltration is purposed to produce the better quality of refined yellow grease than refined yellow grease from adsorption or ultrafiltration process only.

2.1. Materials
Materials used in this study were yellow grease (used cooking oil), bagasse, technical H₃PO₄, distillate water, Polyethersulfone (PES), N-Methyl-2-pyrrolidone (NMP), ethanol 95%, KI, KOH, IBr₂, Na₂SO₃, glacial acetic acid, chloroform, amylum 1%.

2.2. Methods
The processes of yellow grease refining are schematically arranged as shown on figure 1 and figure 2.
2.2.1 **Manufacture of adsorbent from activated bagasse.** Bagasse was dried in advanced with sunlight. Then, bagasse was cut in 5 mm size and was then carbonized using tubular furnace for 2 hours at 350°C. After that, bagasse carbon was finely grounded and screened using screener until it sized 100 mesh. The bagasse carbon was then chemically activated with H₃PO₄ 12.5%, and stirred for 4 hours.

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**Figure 1.** Flow chart of adsorbent manufacture and adsorption process.

**Figure 2.** Flow chart of membrane manufacture and ultrafiltration process.
4 hours at 60 rpm and 80°C. Next, bagasse was filtrated using a 5 micron filter paper and washed until its pH is neutral. Finally, the activated carbon was dried in oven at 105°C for 2 hours [6].

2.2.2 Processing yellow grease with adsorption process using adsorbent from bagasse. In adsorption stage, several variation of bagasse mass was fed into 200 ml of yellow grease and stirred for 60 minutes at 60 rpm. Sample was then filtrated using a 5 micron filter paper to separate yellow grease from adsorbent, and then the sample’s acid number, peroxide number, iodine number, and water content were analyzed. Adsorption result with best condition will be further processed using membrane.

2.2.3 Manufacture of Polyethersulfone (PES) membrane with phase inversion by immersion precipitation method. Dope solution was made by solving Polyethersulfone (PES) and N-Methyl-2-pyrrolidone (NMP) with polymer concentration by 15 wt %, 20 wt %, and 25 wt % of weight. Dope solution was casted on glass plate with 200 µm of thickness, and then it went through solvent evaporation process for 1 minute before coagulated in coagulation bath filled with non-solvent (distilled water). After the membrane was prepared, the permeability test was done using deionized distilled water at various transmembrane pressures (TMP) which are 0.5; 1; 1.5; and 2; 2.5 Bar. While the membrane used in yellow grease refining is classed as ultrafiltration membrane.

2.2.4 Processing of yellow grease resulted from adsorption process by using ultrafiltration membrane. Yellow grease produced from adsorption with best condition was then processed with ultrafiltration membrane process. Feed of yellow grease was flown through dead-end system membrane module with transmembrane pressure variation by 0.5; 1; 1.5; 2; and 2.5 Bar. Permeate resulted was then analyzed to know its acid number, peroxide number, iodine number, and water content.

3. Result and Discussion

3.1. Analysis of Initial Characteristics of Yellow Grease

In this study, the initial characteristics of yellow grease were determined as a comparison between the qualities of yellow grease before and after refined. Characteristics of yellow grease were described by several numbers that had been determined from calculation result with several analyses conducted. Comparison of initial characteristic of yellow grease with predefined SNI standard can be seen on Table 1.

| Characteristic       | SNI                              | Analysis results                  |
|----------------------|----------------------------------|-----------------------------------|
| Acid Number          | Max. 2 Mg KOH / g                | 2.68 Mg KOH / g                   |
| Peroxide Number      | Max. 2 Meq / kg                  | g                                 |
| Iodine Number        | 45-46                            | 5.97 Meq / kg                     |
| Water content        | Max. 0.3 %                       | 51.48                             |
|                      |                                  | 1.29 %                            |

From table 1 It can be seen that yellow grease quality was degraded because its acid number, peroxide number, iodine number and water content were not up to or above value interval that has been predefined in SNI regulation. It was caused by the repetitive use of oil that the oil quality was degraded.
3.2. Analysis of Yellow Grease Characteristic in Adsorption Stage

The adsorption step is a preliminary treatment of yellow grease purifications. This step was conducted by varying of amount of mass of adsorbent, then the effect of it on yellow grease characteristics were investigated. The results of characteristic analyses of yellow grease purified are shown in Figure 3.

![Figure 3](image)

**Figure 3.** Characteristic of Yellow Grease from Adsorption Process (a) Acid Number, Peroxide Number, Water Content; and (b) Iodine Number.

Figure 3 describe that adsorption process could increase the quality of yellow grease, compared to its quality before the adsorption process was performed. The values of acid number, peroxide number, iodine number, and water content on the best condition, with 2 grams of adsorbent and 200 mL oil, were 2.55 MgKOH/g; 4.19 Meq/kg; 48.02; and 0.27% respectively.

3.3. Membrane Characterization

Membrane characterization can be done by determining membrane permeability coefficient. Permeability coefficient of membrane (Lp) is carried out through flux measurement, which is by flowing pure water as feed at various transmembrane pressures (TMP). By plotting transmembrane pressure to the flux values, a linear regression curve will be obtained, where the slope is the permeability coefficient.

| PES membrane   | Permeability Coefficient (L/m².h) |
|----------------|-----------------------------------|
| PES 15 wt %    | 10.03                             |
| PES 20 wt %    | 5.414                             |
| PES 25 wt %    | 1.592                             |

According to permeability coefficient of membranes, PES membrane with concentration by 15 wt% is classified as ultrafiltration membrane, while PES membranes with 20 wt % and 25 wt % concentration are classified as nanofiltration membrane. Classification of separation process types of these membranes is based on the range of permeability coefficient for each separation process type. Permeability coefficient of ultrafiltration membrane is ranged between 10-20 L/m².h at operating pressure range between 1 to 5 bar, while the coefficient of Nano filtration membrane is ranged from 1.4 to 12 L/m².h at operating pressure range between 5 to 20 bar [7].
3.4. Analysis of Yellow Grease Characteristic in Ultrafiltration Stage

Ultrafiltration is an advanced step of yellow grease processing after finishing the adsorption stage. Yellow grease sample used in this stage was oil with the best characteristic resulted from adsorption process. Analysis of yellow grease permeate characteristic was also performed for the acid number, peroxide number, iodine number, and water content. The following is the chart of yellow grease characteristic resulted from ultrafiltration process at various transmembrane pressures.

After finishing ultrafiltration process using PES membrane 15 wt %, characteristics of yellow grease including acid number, peroxide number, iodine number, and water content were decreasing along with the increase of transmembrane pressure.

**Free Fatty Acid (FFA).** Based on Figure 4 (a), acid number is decreasing as the increase of transmembrane pressure. The highest acid number was obtained at 0.5 bar pressure, which is 2.8 Mg KOH/gr, and the lowest was obtained at 2.5 bar pressure, which is by 1.12 Mg KOH/gr. Compared to the one resulted from adsorption process, the acid number was decreased at ultrafiltration process. It is because the free fatty acids from yellow grease in the form of dimer and trimer are retained by the membrane whose pore size is smaller than fatty acid molecule size. In addition, the higher transmembrane pressure, the more acid number in yellow grease to decrease. This may be due to the increasing driving force (pressure) that cause an increase in the density of membrane material (compaction) so as to reduce the flux and diffusion of dissolved material through membrane [8]. Flux value is always inversely proportional to the membrane rejection, so the decrease of acid number in yellow grease is because the membrane rejection towards free fatty acid molecules is increasing.

**Peroxide Value.** According to Figure 4 (a), it is seen that peroxide number is also decreasing along with the increase of transmembrane pressure. The decrease of peroxide number in ultrafiltration stage is because peroxide has size that relatively bigger that membrane pore size, so peroxide molecule cannot pass through membrane pores [2]. As well as acid number, the decrease of peroxide number along with the increase of transmembrane pressure is also caused by compaction phenomenon in membrane due to the increase of driving force (transmembrane pressure) that cause the membrane material density to increase and decrease the flux and diffusion of dissolved material through membrane [8].

**Iodine Value.** Iodine number shows unsaturation level of oil and relates to the amount of double bond contained in fatty acid or oil. The more double bond contained in oil, the higher iodine number in it and vice versa [2]. Yellow grease has very low iodine number. This is because to the amount of double bond in used cooking oil is getting smaller due to the high-temperature heating or oxidation reaction that generate free fatty acid, alcohol, aldehyde, free radicals, and single bond [9]. According
to Figure 4 (b), iodine number is decreasing as the increase of transmembrane pressure. This is caused by the more short-chain free fatty acids that can pass through membrane pores due to the increase of given driving force (pressure) that the saturated fatty acid content in yellow grease is still high. Thus, one can say that ultrafiltration of yellow grease using membrane has not been able to increase iodine number [2].

**Water Content.** Water is an undissolved impurity in oil and can be separated through filtration. According to Figure 4 (a), water content in yellow grease resulted from ultrafiltration tends to be stable against transmembrane pressure, where the water content is ranged between 0.02% - 0.05%. Water content in yellow grease resulted from ultrafiltration is significantly reduced, compared to water content in initial sample of yellow grease. Ultrafiltration of yellow grease using PES membrane can reduce water contained in yellow grease. It is because separation process by using membrane PES - which has hydrophobic nature - is based on the difference of membrane wettability by fluids. When water particles are in contact with membrane matrix, they will be trapped or bonded on the membrane surface that they cannot escape through membrane pores [10]. Hydrophobic membrane is easily wetted by oil, so the use of hydrophobic membrane in separating water contained in yellow grease can effectively increase the efficiency of separation process [8].

Recapitulation of the characteristics of yellow grease refined from adsorption and ultrafiltration can be seen on the following Table 3.

| Parameters          | SNI Initial sample | Refining Stages | Refining Efficiency (%) |
|---------------------|--------------------|-----------------|-------------------------|
|                     |                    | Adsorption a    | Ultrafiltration b       | Adsorption | Process Combination c |
| Acid Number (MgKOH/g) | 2                  | 2,68            | 2,55                    | 1,12       | 4,85                  | 58,21 |
| Peroxide Number (meq/kg) | 2              | 5,97            | 4,19                    | 1,8        | 29,82                 | 69,85 |
| Iodine Number       | 45-46              | 51,48           | 48,02                   | 41,36      | 6,72                  | 19,66 |
| Water Content (%)   | 0,3                | 1,29            | 0,27                    | 0,02       | 79,07                 | 98,45 |

a Adsorption with 2 grams adsorbent (bagasse) mass.
b Ultrafiltration with PES 15 % and 2,5 bar transmembrane pressure.
c Process combination of adsorption and ultrafiltration.

According to the recapitulation result, it can be seen that the characteristics of yellow grease resulted from ultrafiltration has reduction in acid number, peroxide number, iodine number, and water content, compared to the result obtained in adsorption stage. Characteristics of oil that meet the SNI standards are acid number, peroxide number, and water content, while the iodine number has not meet the range set by SNI. The change of colour of yellow grease before and after processing can be seen on Figure 5.
Figure 5. (a) Yellow grease; (b) Yellow grease resulted from adsorption process (c) Yellow grease resulted from combination of adsorption and ultrafiltration membrane process.

4. Conclusion

Variation of adsorbent mass in adsorption stage had effect on yellow grease characteristic. Adsorbent mass that was efficient to use for yellow grease preliminary treatment was by 2 grams, with acid number, peroxide number, iodine number, and water content decreased to 2.55 Mg KOH/gr; 4.19 Meq/kg; 48.02; and 0.27% respectively. Transmembrane pressure that was efficient in increasing yellow grease characteristics in ultrafiltration membrane refining process was at 2.5 bar, which could reduce the value of acid number, peroxide number, and water content respectively to 1.12 Mg KOH/gr; 1.8 Meq/kg; and 0.02%. The yellow grease’s acid number, peroxide number, and water content from the processes combination has meet the range set by SNI, while the iodine number has not.

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