Catalytic transfer hydrogenation of castor oil using glycerol-based reaction

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Abstract. A catalytic transfer hydrogenation of castor oil using glycerol-based is a process of adding hydrogen to the castor oil to produce hydrogenated castor oil with the addition of 10% Pd/C as the catalyst and glycerol as a hydrogen donor. The reaction occurred at the reaction temperature of 178°C for an hour. To prove whether glycerol can be one of the hydrogen donors like limonene that is commonly used, the research started by using pure glycerol as the hydrogen donor and as a control to determine the protocol. A direct heating apparatus connected with a reflux system was used for this experiment. The result from FTIR along with the melting point shows the formation of hydrogenated castor oil from this reaction. The increment in melting point value and the absence of C=C peak (1655.79 cm⁻¹) from FTIR spectrum shows that the catalytic transfer hydrogenation successfully occurred. The melting point of the hydrogenated castor oil is 65°C and the melting point of castor oil is -7°C. Therefore, it was proven that, the glycerol can be used as the hydrogen donor for the castor oil for a catalytic transfer hydrogenation reaction.

1. Introduction

Castor oil is a non-edible vegetable oil that is extracted from castor seed, also known as Ricinus communis [1-3]. The castor bean plant comes from the family of Euphorbiaceae and can produce around 40 to 50% oil when cold-pressing method of extraction is used [2]. Nowadays, castor oil plant, is cultivated on a commercial scale all over the world [2]. India is currently the largest exporter of castor oil in the world and Asian countries are also get interested in castor oil since this non-edible vegetable oil is the only vegetable oil that contain high amount of ricinoleic acid, which makes it different from others. Castor oil contains around 80 to 90% of ricinoleic acid, 3 to 6% linoleic acid, 2 to 4% oleic acid and 1 to 5% saturated fatty acids [4-6]. The surrounding during the plant growth might affect the resulting amount of the oil extraction whereby according to Mubofu [1], in order to extract high amount of oil, the plant needs an environment with a temperature around 20°C and 30°C with low humidity throughout the growing seasons, a deep soil, moderately fertile, slightly acidic, well drained, and a sandy loam. Besides that, method of oil extraction is also one of the factors that affects the amount of oil extracted from the castor seed. According to Mutlu et al. [2], the most suitable method of oil extraction in order to have high amount of oil yield is the combination of two methods which are hot pressing by using a hydraulic press and followed by the solvent extraction method.

Castor oil with its unique characteristics, which is high content of ricinoleic acid makes it commercially valuable in the production of soaps, lubricants, and coatings [3]. Hydrogenation is one of the methods that can be used to optimize the use of castor oil in the industry. Hydrogenation is the addition of hydrogen to each of the carbon atom of the double bond [7]. Catalytic transfer hydrogenation is the alternative method to hydrogenate the castor oil with the presence of a catalyst and hydrogen donor at mild conditions. The early stage of the hydrogenation process was run by using high temperature and pressure, which need a special equipment for the reaction due to its tendency to explode. Therefore, catalytic transfer hydrogenation was established to reduce the risk of an explosion with the presence of a metal catalyst, hydrogen donor at low temperature and atmospheric condition. According to Fitri et.al, there are a few advantages of catalytic transfer hydrogenation whereby it does not require hazardous
pressurized H₂ gas and the major side product can be recycled [8]. Theoretically, the hydrogenation process occurs on the catalyst’s surface whereby the hydrogen atom attached on the catalyst’s surface by a chemical reaction where unpaired electrons on the surface of the metal pair with the electrons of hydrogen and bind the hydrogen to the surface and followed by alkene on the surface [7]. Then, the hydrogen atom will transfer to the alkene and followed by the second hydrogen atom. Finally, after two hydrogen atoms have been added to the same side of the double bond, the saturated alkane will form, and it will detach from the metal catalyst.

Due to a massive increase of glycerol in our industry ever since the rapid production of biodiesel, researchers started to discover the novel used of glycerol. According to Tavor et al. [9], glycerol can be used as a hydrogen donor for olefin in catalytic transfer hydrogenation process. Therefore, the objective of this research work is to find out the best protocol to be practiced towards the use of glycerol as a hydrogen donor in catalytic transfer hydrogenation in producing hydrogenated castor oil.

2. Methodology

2.1. Chemical and reagent
Commercial castor oil was collected from Crude Oil Fouling Research Centre in Universiti Teknologi PETRONAS (UTP). Palladium on carbon (Pd/C, 10% w/w dry basis) was used as the catalyst in this reaction. Glycerol (99.5% pure) and R-(+)-Limonene, 94% were purchased from Avantis Laboratory Supply as hydrogen donors for the catalytic transfer hydrogenation process. Dichloromethane (Merck 106050) and methanol (99.9% pure) were used for the purification procedure after the reaction.

2.2. Hydrogenation procedure
The 10% w/w of Pd/C catalyst, castor oil and glycerol were used for the catalytic transfer hydrogenation (CTH) reaction. The molar ratio of castor oil to glycerol adopted from the studies by Martinelli et al. [11] was 1:3 and the amount of catalyst used was corresponding to 1 molar% Pd in relation to the double bond of castor oil. The catalyst, castor oil and hydrogen donor were mixed together in a one-neck round bottom flask with a conventional heat source and connected to a reflux system. The mixture was heated up to 178ºC for an hour. A K-type thermocouple was used to monitor the temperature and control the heating to ensure a constant temperature. The reaction mixture was cooled down to room temperature and the viscosity of the mixture increased. About 5 to 10 mL of dichloromethane, which work as solvent was added to the flask and stirred for 5 minutes. Then, the mixture was filtered to remove the catalyst and methanol was later added in excess for further purification. The same procedure was repeated with limonene as the hydrogen donor instead of the glycerol. The same ratio of castor oil to glycerol was maintained for limonene. The melting point of the product was analyzed by using the melting point apparatus (model: SMP3) provided in the department.

2.3. FTIR analysis
FTIR was used to identify the possible functional groups that were present in castor oil and hydrogenated castor oil (HCO) from glycerol and limonene as the hydrogen donor. The spectra used for the samples was within 4000 cm⁻¹ to 450 cm⁻¹ wavelengths by using 64 scans.

2.4. H-NMR analysis
The H-NMR spectra for the samples were recorded on a NMR spectrometer operating at 500 MHz at room temperature using CDCl₃ as solvent. The method reported by Martinelli et al. [11] was adopted for this analysis.

3. Result and discussion

This experiment was performed to produce hydrogenated castor oil (HCO) by using glycerol as one of the green solvents and hydrogen donors (Figure 1) as mentioned by Wolfson et al. [10]. Besides that,
the experiment aims at identifying the right protocol for the catalytic transfer hydrogenation process by using glycerol as hydrogen donor. Therefore, after a few trial runs of experiment, the right protocol was identified whereby the researcher needs to place the catalyst first followed by the castor oil and finally the hydrogen donor, which is the glycerol will be added. The metal catalyst, Pd/C used provided a new pathway for the reaction to occur at a lower temperature [7].

**Figure 1.** Structure of hydrogenated castor oil produced from hydrogenation of castor oil

The HCO was produced when the reagents were added in the reaction procedure in the correct order. As mentioned in the research paper by Martinelli et al. [11], when the oil was added to the catalyst after the hydrogen donor, the oil remained unreacted since the active site of the catalyst became unavailable because was blocked by the hydrogen donor disproportionation reactions. The hydrogenation process successfully occurred when white solid powder (Figure 2) is formed during the reaction and the product turned to solid when it reached room temperature. The mixture turns to brownish liquid (as portrayed in Figure 3) indicates that the reaction failed as a result of wrong order of reagents addition during the reaction. The formation of brown coloration is due to undesirable reaction resulting in the formation of other products. For further confirmation, the melting point and possible functional groups that were present in the samples were analyzed.

**Figure 2.** Pictorial view of hydrogenated castor oil produced from hydrogenation of castor oil

**Figure 3.** Brownish liquid for shown unsuccessful reaction

### 3.1 Melting point
The melting point for each sample was tested for three times and the average value was recorded in Table 1. From the result collected, it has shown that the melting point of the hydrogenated products were higher compared to the melting point of castor oil. The melting point of castor oil is -3 to -7°C which is very close to that reported by other researchers [3, 12]. The increase in melting point of the hydrogenated
Castor oil occurred due to the properties of the castor oil that changed from unsaturated fatty acid to saturated fatty acid with the addition of hydrogen atom to the structure bonds. According to Nassu et al. [13], the hydrogenation process formed the trans and positional isomer to the structure bonds, which resulted in the formation of non-intersoluble triglyceride thus raising the melting point of the hydrogenated products. The melting point obtained for the hydrogenated castor oil produced in both cases agree closely to the values reported in the literature (67.0–84.1°C) [16]. The hydrogenation process itself is defined as a conversion process of liquid oils into semi-solid substances with specific melting values and partially hydrogenated oils, which improved its stability [14].

| Sample                              | Melting point value (°C) |
|-------------------------------------|--------------------------|
| Hydrogenated castor oil – glycerol  | 74.7                     |
| Hydrogenated castor oil-limonene    | 77.8                     |

3.2. FTIR analysis
The infrared spectra of castor oil and hydrogenated castor oil from glycerol as the hydrogen donor is shown in Figure 4. A broad peak formed at 3400.89 cm\(^{-1}\) for castor oil spectra is attributed to the stretching vibration of ─OH in fatty chain that was contributed by the presence of hydroxyl group at C-12 position in castor oil [15]. Ricinoleic acid as the main fatty acid in the castor oil plays its role whereby it carries a secondary ─OH group on its 12 carbon which will increase the oil viscosity to a high extent due to the hydrogen bonding [16, 17]. The huge band area suggests the high concentration of ─OH [18]. According to Zajcew [19], the hydroxyl content will be reduced after the hydrogenation process and for this experiment it can be seen from the reduction of band area of the vibration of ─OH at the HCO-glycerol spectra in Figure 4. The sharp peak formed at 3007.92 cm\(^{-1}\) is attributed to the C-H stretching vibration of the cis-double bond (=CH) and the other two peaks formed at 2925.79 and 2854.96 cm\(^{-1}\) shows the vibration of aliphatic CH\(_2\) group of symmetric and asymmetric stretching. The strong peak formed at 1743.42 cm\(^{-1}\) for the castor oil attributes to the ester carbonyl functional group of the triglycerides and the most important peak was the peak that formed at 1655.69 cm\(^{-1}\) which represents the carbon double bond (C=C) stretching vibration of cis-olefins. From the HCO-glycerol spectra, the disappearance of a weak peak at 1655–1650 cm\(^{-1}\) was attributed to the absence of C=C functional group after the hydrogenation. According to Alwaseem [15], the weak signal at 1650 cm\(^{-1}\), attributed to the C=C bond disappeared after the hydrogenation process. The peaks shown at the fingerprint region (1241 – 1167 cm\(^{-1}\)) represent the stretching vibration of C-O-C in the triglyceride section of castor oil and the strong sharp peak at 724.68 cm\(^{-1}\) shows the overlapping of the CH\(_2\) rocking vibration and the out of plane vibration of cis-distributed olefins.
Figure 4. Spectra of castor oil and hydrogenated castor oil (HCO) by using glycerol as hydrogen donor.

Figure 5 shows the spectra of HCO-glycerol and HCO-limonene and it seems as if like there was not much difference in terms of the functional group that is present in the hydrogenated product. From this result, it is shown that glycerol has the potential to replace limonene in the hydrogenation of castor oil thus reducing the production cost of hydrogenated castor oil by using catalytic transfer hydrogenation process, since glycerol is a low-cost byproduct of transesterification of oil.

Figure 5. Spectra of hydrogenated castor oil using glycerol and limonene as hydrogen donor.

3.3. NMR spectra analysis
H-NMR spectrum of castor oil in Figure 6 showed the presence of tertiary proton –CH$_2$CHCH$_2$– from glycerol structure backbone, which appear at chemical shift, δ 5.2-5.6. The methylene proton of the –CH$_2$-CHCH$_2$– backbone appear at δ 4.1-4.4 and the tertiary hydrogen adjacent to the hydroxyl proton in fatty acid chain appears at δ 3.5-3.6 ppm [20].
After the hydrogenation reaction occur, the tertiary carbon at 5.2-5.6 ppm should disappear upon the completion of hydrogenation process. However as seen in Figure 7, the peaks did not disappear completely. In a good note, the intensity of the peaks at the mentioned chemical shift decreased significantly indicates that the hydrogenation process did occur during the reaction. The small residue peak around 5.2 ppm, can be attributed to unreacted material during the hydrogenation process [21].

4. Conclusion

Catalytic transfer hydrogenation process is a process of adding hydrogen to the structure in the presence of a catalyst and hydrogen donor. This reduces the number of carbon double bond. This process converts the unsaturated hydrocarbon to saturated hydrocarbon at mild condition, which is at a low temperature and pressure. In this study, glycerol and limonene as the hydrogen donor were used in the catalytic hydrogenation process of castor oil, to ascertain the potential of glycerol as hydrogen donor in the catalytic hydrogenation of castor oil. Hydrogenated castor oil was produced with glycerol as hydrogen donor during the process as confirmed by the increase the melting point of the product (hydrogenated castor oil) to 74.7°C for glycerol and 77.8°C for limonene. The acceptable order of addition of reagents for the hydrogenated castor oil using glycerol is firstly the addition of the catalyst followed by the castor oil and finally the hydrogen donor, which is the glycerol. Besides that, the absence of C=C peak (1655.69 cm⁻¹) from the hydrogenated spectra proves that the hydrogenation process occurred during the reaction.
This is a good indication of the potentials of crude glycerol from transesterification process hydrogen donor thus creating and avenue for utilization of crude glycerol from the rapid production of biodiesel.

5. References

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